Sunday Afternoon, November 6, 2022

Biomaterials Plenary Session & Flash Poster Session
Room 318 - Session BP-SuA

Biomaterials Plenary Session: Programmable Biologic Materials (ALL-INVITED SESSION)

Moderators: Caitlin Howell, University of Maine, **Markus Valtiner**, Vienna University of Technology, Austria

4:20pm **BP-SuA-5 Enhancing the Programmability of Engineered Extracellular Matrices with Sequence Specific Peptoids***, Adrianne M. Rosales,* The University of Texas at Austin **INVITED**

Hydrogel substrates have garnered intense interest as engineered extracellular matrices due to their tailorable mechanics and degradability. These substrates can be composed of naturally derived materials (e.g., collagen) or synthetic materials (e.g., poly(ethylene glycol). Synthetic materials are attractive due to their known chemical compositions and scalability, but the challenge with their use lies in the lack of complexity as compared to biological systems, especially with regard to sequence-specific bioactivity. Hence, our work aims to enhance the programmability of synthetic hydrogel biomaterials by using precise polymer architectures, specifically with a class of materials called peptoids. Here, we describe our efforts to control two key properties of hydrogel substrates with peptoid functionality: 1) bulk mechanics and 2) enzymatic degradability. Tailoring these features is essential for regulating the interface of hydrogel substrates with adhered cells for efficacious cell manufacturing and tissue engineering platforms.

Drawing inspiration from semiflexible biopolymers, we achieved control over the mechanics of hydrogel substrates by controlling chain structure with peptoid cross-linker sequence. Specifically, helical peptoids increased the shear moduli of hydrogels due to increased chain stiffness as compared to non-helical peptoids, while keeping all other hydrogel parameters fixed. This strategy decoupled bulk mechanics of the substrate from the network connectivity, allowing for investigation of mechanical effects on adhered mesenchymal stromal cell (MSC) behavior. We found that MSCs adhered on soft substrates secreted higher levels of indoleamine 2,3-dioxygenase (IDO), an immunomodulatory enzyme necessary for enhanced cell performance. Furthermore, we examined the ability of peptoids to tune hydrogel degradability via proteolysis. We substituted peptoids into key sites of proteolytically degradable substrates, enabling a tailored material response to matrix metalloproteinases secreted by cells. Overall, our results suggest that sequence control of synthetic peptoids may provide effective strategies for expanding the functionality of biomaterial scaffolds for tissue engineering and regenerative medicine, particularly with respect to mechanics and degradation in complex biological environments.

5:00pm **BP-SuA-7 New Biomaterials and Bio-inspired Materials from Polyelectrolyte Complexation***, M. Tirrell,* University of Chicago*; **Yun Fang**,* The University of Chicago **INVITED**

Nature exploits all available covalent and non-covalent interactions for unparalleled spatiotemporal control over hierarchical length scales of macromolecular and supramolecular structure. The complex interplay of electrostatic and other non-covalent interactions of charged macromolecules still poses many open questions that will require broad collaboration among the life and physical sciences, as well as input from the engineering disciplines to drive toward new solid-state structures and useful materials. Scientific questions related to the physics of electrostatic self-assembly and to its role in biology will be discussed. Recent advances in understanding and biomedical applications of polyelectrolyte complex micelles will be presented.

5:40pm **BP-SuA-9 BID Flash Poster Session: Oral Presentations***,*

5:40. BI-TuP-2 - Hannah Omeoka

5:43: BI-TuP-8 - Juhi Jaiswal

5:46: BI-TuP-12 - Ainslie Allen

5:49: BI-TuP-6 Shahidul Alam Mohammad

Nanoscale Science and Technology Plenary Session
Room 304 - Session NSP-SuA

Nanoscale Science and Technology Plenary Session (ALL-INVITED SESSION)

Moderator: David Czaplewski, Argonne National Laboratory

3:00pm **NSP-SuA-1 Adventures in Nanofabrication and Manufacturing, from Electron-Beam Lithography to DNA: Science, Technology, and Lessons Learned***, **James Liddle**,* National Institute of Standards and Technology (NIST) **INVITED**

Over the past three decades, our ability to manipulate and control matter at the nanoscale has advanced dramatically, with investments and progress driven by both the demands of the semiconductor industry and by the potential for nanotechnology to deliver powerful new capabilities in areas as diverse as medicine and energy.While we now have a myriad of nanofabrication techniques at our disposal, determining when and how to implement them in manufacturing is one of the most complex and daunting challenges encountered in research and development.In this talk, I will illustrate the tortuous (and torturous) path from nanofabrication concept to nanomanufacturing implementation through two examples – electron-beam lithography and nucleic acid nanofabrication – taking full advantage of the clarity of vision afforded by hindsight.In both cases, much of the original motivation for research and development came from the desire to solve the *perceived* problem that, in microelectronic manufacturing, ever-diminishing feature sizes would collide with the physical limitations of the incumbent technology – optical lithography – leading to an abrupt end to Moore's Law.As the continued dominance of optical lithography, and its successor, EUV, attest, this analysis was flawed.As I will show, the inability to formulate the correct problem statement, albeit in the context of a rapidly evolving technological environment, led to a number of false starts and dead ends.However, over the course of time, a lot of time, the application areas for which these two technologies are well-suited has come into focus, and much of the knowledge gathered during the course of a stochastic exploration of possible application areas has turned out to be critical in maturing them to the point of manufacturing readiness.Ultimately, the lessons to be learned are that predicting the trajectory of a new technology is not for the faint of heart, and bringing one to market requires constant critical examination of the problem being solved in the context of the competitive landscape, the flexibility to change direction, and unwavering persistence.

2D Materials Technical Group
Room 303 - Session 2D+EM-MoM

2D Materials: Electronic, Mechanical, and Optical Properties

Moderator: Sarah Haigh, University of Manchester, UK

8:20am **2D+EM-MoM-1 Scanning Tunneling Spectroscopy of 2d Electronic Materials – from Monolayers to Complex Heterostructures***, **Chih-Kang (Ken) Shih**,* Department of Physics, The University of Texas at Austin **INVITED**

Atomically thin, single-crystalline 2D electronic materials have recently emerged, offering a remarkably wide range of building blocks of nanostructures, ranging from metals (e.g. graphene), large gap insulators (BN), to semiconductors (transition metal dichalcogenides and black phosphorous). One key advantage of these van der Waals materials lies in the flexibility of stacking different types of materials to form heterostructures, providing a design platform for achieving novel device functionality.With the ability to probe electronic structures with atomic resolution, scanning tunneling microscopy/spectroscopy (STM/S) has played a crucial role in advancing our understanding of the electronic structures of 2D electronic materials and their heterostructures.

In this talk, I will present a comprehensive combination of different modes of scanning tunneling spectroscopy beyond the conventional constant height tunneling spectroscopy.I will use a few examples to show how such comprehensive investigations provide an in-depth understanding of the electronic structure evolutions from monolayer to complex heterostructures (including moire superlattices and beyond).

9:00am **2D+EM-MoM-3 Strain and Charge-Transfer at the Device Relevant Interface Between Single Layer MoS$_2$ and Gold: In-Situ Raman Study***, **Stephanie Lough**, J. Thompson,* University of Central Florida*; R. Rao,* Air Force Research Laboratory*; M. Ishigami,* University of Central Florida

Next-generation technology nodes will reach the sub-nanometer range via the introduction of ultra-thin and short-channel devices. Traditional semiconductors such as silicon (Si) suffer from device-degrading effects such as roughness-induced scattering or short-channel effects at this size scale. Two-dimensional transition metal dichalcogenides (2D TMDs) do not suffer from these effects. Therefore, they could be candidate materials for the next-generation nodes. Single-layer molybdenum disulfide (SL-MoS$_2$) devices exhibit carrier mobilities exceeding that of Si-based devices with similar thicknesses, but suffer from high contact resistance, reducing their utility in device technologies. Our previous results show that the physics at the interface between SL-MoS$_2$ and gold (Au) is complex and that thermal annealing (TA) under certain conditions could lead to lowered contact resistance by direct chemical hybridization and/or doping.

We performed detailed *in situ* Raman spectroscopy of exfoliated SL-MoS$_2$ on Au during and after annealing at temperatures ranging from room temperature (RT) to 300 °C in Ar. This revealed doping and mechanical strain induced in the SL-MoS$_2$ by the underlying Au layer. Using peak deconvolution, we identify the presence of two sub-peaks comprising each of the well-known MoS$_2$ fingerprint peaks (A_{1g} and E_{2g}), consistent with previous studies. The ratio of intensities and relative shifting of the sub-peaks indicates a strong interaction between the MoS$_2$ and the Au layer, which could be due to hybridization between the MoS$_2$/Au. The well-known Si peak at 520 cm^{-1} diminished as the temperature was increased. As such, we conclude that the MoS$_2$ delaminated from the Au layer at elevated temperatures. The coupling between the Au and MoS$_2$ was reestablished upon cooling to RT after annealing as indicated by the reappearance of the Si peak. Further, as the MoS$_2$ was annealed at progressively higher temperatures, it became increasingly electron-doped by the Au with the strain remaining constant at 1% in tension.

Our data shows that TA and cooling of the interface between SL-MoS$_2$ and Au produces stronger coupling, suggesting an increased level of hybridization between the MoS$_2$/Au. The hybridization results in a nearly charge-neutral MoS$_2$-Au heterostructure, indicating that TA could be a path toward achieving intrinsic contacts for device applications. Finally, the strain between these surfaces remains unchanged upon annealing, implying that annealing promotes stronger coupling between SL-MoS$_2$/Au, without increasing strain. Thus, annealing presents an ideal route towards generating charge-neutral MoS$_2$/Au contacts with minimal interfacial strain.

9:40am **2D+EM-MoM-5 Optical and Electrical Investigation into HfS$_2$ Oxidation Mechanisms***, I. Chirca, A. Almutairi, **Stephan Hofmann**,* University of Cambridge, UK

2D layered materials are emerging as potential candidates for energy-efficient conventional devices, as well as new memristive and neuromorphic device architectures. The focus to date has been on new semiconductor materials, particularly transition metal dichalcogenides (TMDs). Yet, feasible technology, especially in the optoelectronics field, relies on clean interfacing, particularly to a suitable dielectric. HfS$_2$ is one of the few materials that offer a native oxide conversion pathway, previously demonstrated in various experimental set-ups. Here we explore the oxide formation kinetics on HfS$_2$ layers and the achievable interface quality in HfS$_2$/HfO$_x$ devices.

To accomplish this, we employ several HfS$_2$ oxidation methods, from thermal to plasma and pulsed water vapour exposure, and compare the electrical switching behaviour of MIM and MIS device structures while characterizing their dielectric properties via spectroscopic ellipsometry. The oxidative behaviour of HfS$_2$ and the buried HfS$_2$/HfO$_x$ interface are observed optically using a combination of reflectance spectra and ellipsometric modelling. In order to determine the viability of such an approach for device fabrication, the natively grown HfOx is benchmarked against ALD grown hafnia.

Thus, our study is a step towards finer control of interface quality in HfS$_2$/HfO$_2$ devices through calibration of the native oxidation pathway.

10:40am **2D+EM-MoM-8 Electrical Characterization of β-In$_2$Se$_3$ Thin Films Synthesized via Molecular Beam Epitaxy***, **Cooper Voigt**,* Georgia Institute of Technology, USA*; B. Wagner,* Georgia Tech Research Institute*; E. Vogel,* Georgia Institute of Technology, USA

β-In$_2$Se$_3$ is a two-dimensional semiconductor that has long been believed to have a centrosymmetric crystal structure. α-In$_2$Se$_{3-}$ is a closely related, two-dimensional, ferroelectric semiconductor [1,2] and has shown promise in low-power, neuromorphic electronic devices [3,4] and transistors [5]. Much work has been devoted to exploring the performance of α-In$_2$Se$_3$ in electronic devices due its unique combination of properties; however large-area thin-film synthesis of α-In$_2$Se$_3$ has not been established. Since 2018 there have been reports of polarization in a β′-In$_2$Se$_3$ phase arising from displacements of the center layer selenium atoms [6–8]; however, these studies have not included any fabrication and characterization of electronic devices. One study from 2018 claims deposition of large-area, ferroelectric In$_2$Se$_{3-}$ -thin-films via MBE; however, it is difficult to distinguish the α from β phase by the Raman spectra and TEM micrographs provided. Earlier this year, ferroelectric behavior was reported in transistors fabricated from metal-organic chemical vapor deposition (MOCVD) β-In$_2$Se$_3$ [9]. If β-In$_2$Se$_3$ does truly exhibit ferroelectric ordering, it would be a very promising material for low-power transistors and neuromorphic electronic devices.

In this study, we demonstrate molecular beam epitaxy (MBE) synthesis of β-In$_2$Se$_3$ thin-films and electrical characterization of β-In$_2$Se$_3$ transistors. We link processing parameters such as synthesis substrate temperature, and Se/ In flux ratio to resulting β-In$_2$Se$_3$ electrical properties and device performance.

[1]M. Küpers, et. al., Inorg. Chem. **57**, 11775 (2018).

[2]J. Xiao, et. al.,Phys. Rev. Lett. **120**, 227601 (2018).

[3]B. Tang, et. al., ACS Appl. Mater. Interfaces **12**, 24920 (2020).

[4]L. Wang, et. al., Adv. Funct. Mater. **29**, 1 (2019).

[5]M. Si, et. al., Nat. Electron. **2**, 580 (2019).

[6]S. Li, et. al., Sci. Adv. **4**, eaar7720 (2018).

[7]F. Zhang, et. al., ACS Nano **13**, 7, 8004–8011 (2019).

[8]Z. Zhang, et. al., Adv. Mater. **34**, (2022).

[9]S. Lee, et. al., 2D Mater. **9**, 025023 (2022).

[9]S. M. Poh, et. al., Nano Lett. **18**, 6340 (2018).

[10]S. Lee, et. al., 2D Mater. **9**, 025023 (2022).

11:00am **2D+EM-MoM-9 Mechanics of Pristine and Pyrolysed Carbon Nanomembranes (CNMs)*, André Beyer*,** *F. Paneff, X. Zhang, A. Gölzhäuser,* Bielefeld University, Germany

The discovery of graphene has triggered a great interest in inorganic as well as molecular two-dimensional (2D) materials. Over the last years, a remarkable progress in the mechanical characterization of free-standing 2D materials was achieved [1]. In this contribution, we compare mechanical characterization of membranes by means of bulge tests and nanoindentation experiments. The bulge test was found to be a reliable method, which is suited for any kind of membrane. Nanoindentation was found to be suited for a number of membrane types while others entail a high risk of rupturing. With these two methods, a number of different pristine and pyrolysed carbon nanomembranes (CNMs) were examined. CNMs form by irradiation induced cross-linking of molecular layers e.g. self-assembled monolayers of terphenylthiol (TPT) molecules. Cross-linking between adjacent molecules was induced by low energy electron exposure. Pyrolysis of CNMs is known to yield nanocrystalline graphene, which is in agreement with the observed stiffening of the membranes. Part of this contribution will be devoted to a comparison of different approaches to analyse pressure-deflection measurement data of bulge tests. A sum of the limits approach is suggested as most precise method that employs an analytic pressure-deflection expression for determining the mechanical properties.

[1] X. Zhang and A. Beyer, Nanoscale 13, 1443 (2021).

11:20am **2D+EM-MoM-10 Interplay between Electronic, Magnetic and Mechanical Properties in 2D Crystals*, Young-Woo Son*,** Korea Institute for Advanced Study, Republic of Korea **INVITED**

In this talk, I will discuss unique aspects of two-dimensional crystals that show intertwined nature between electronic, magnetic, optical properties and structural distortions. First, when a transition metal dichalcogenide (TMD) overlay another TMD forming moire superlattices, the softer one deforms itself to conform the mismatched lattices between them so that the unique whirlpool shaped lattice distortions occur [1]. I will show our recent theoretical and computational study shown that the pair of torsional distortions with the opposite chirality introduce characteristic fuzziness in Raman spectroscopy and interesting excitonic signatures irrespective twist angles. agreeing with experiments very well [1]. Second, a newly synthesized 2D carbon allotrope by linking biphenylene molecules is shown to host interesting type II Weyl fermions together with a possible magnetic orderings [2]. With external mechanical perturbations, our first-principles calculations including self-consistent extended Hubbard interactions reveal the anomalous Lifshitz transition of pair annihilations with merging onto zone-center saddle point.

[1] J. Kim, E. Ko *et al.*, *Nat. Mater.* (2022). https://doi.org/10.1038/s41563-022-01240-2

[2] Y.-W. Son *et al.*, *Nano Lett.***22**, 3112 (2022).

Atomic Scale Processing Focus Topic
Room 317 - Session AP+2D+AS+EM+PS+SS+TF-MoM

Area Selective Processing and Patterning

Moderators: Eric A. Joseph, IBM Research Division, T.J. Watson Research Center, **Adrie Mackus**, Eindhoven University, Netherlands

8:20am **AP+2D+AS+EM+PS+SS+TF-MoM-1 Imperfectly Perfect Materials and/or Processes as a Route for ASD*, Christophe Vallee*,** SUNY POLY, Albany*; M. Bonvalot, M. Jaffal, T. Yeghoyan,* University Grenoble Alpes, LTM, CNRS, France*; N. Posseme, R. Gassilloud, T. Chevolleau,* CEA/LETI-University Grenoble Alpes, France **INVITED**

In recent years, many strategies have been presented to selectively deposit a material on a specific surface (area selective deposition), or space direction (topographically selective deposition). Whatever the selective process developed to this end (inherent delay, surface inhibition, surface activation, super-cycles...), it is expected that a perfect material is perfectly deposited on the surface at stake. However, this most often implies that some imperfect material is thereby deposited on surfaces where no growth is expected. Taking this logic a little further ahead, we can even imagine that it may not be at all necessary to develop perfect ALD processes to achieve ALD-based selective deposits.

In this presentation, we will show how imperfect ALD processes can be developed by working out of the ideal precursor ALD window or regime, to adequately lead to ASD processes. We will also show that the requirements of an ideal growth inhibition of no-growth surfaces can be successfully circumvented for ASD processes. Indeed, the simultaneous deposition of a same material on two differing substrates can lead to inherent discrepancies in the materials quality, that can be advantageously taken into consideration in the development of a localized bottom-up growth strategies by adding a selective etching step.

9:00am **AP+2D+AS+EM+PS+SS+TF-MoM-3 Area Selective Deposition on EUV Photoresist*, Rosanna Robert,*** SUNY College of Nanoscale Science and Engineering*; H. Frost, K. Lutker-Lee,* TEL Technology Center, America, LLC, USA*; C. Vallée,* SUNY College of Nanoscale Science and Engineering

Area selective deposition (ASD) is a key process required for the next generation of nanotechnology. ASD utilizes surface chemistry and reaction modifications to promote growth on one of two different materials. When applying an ASD process to a patterned wafer with both materials exposed, we can selectively grow a film on one surface while blocking growth on the other surface (known as the nongrowth area). One application for ASD is ultra-thin extreme ultraviolet (EUV) photoresist repair to enable continued pitch scaling in the Back End of Line[1]. Pattern transfer fidelity depends on initial line edge roughness (LER) and line width roughness (LWR) values of the EUV resist. Moreover, local critical dimension uniformity (LCDU) for <30 nm critical dimension hole patterning also varies with the initial resist thickness[2]. In this project, we propose to develop an ASD on EUV resists before or alternatively during an etch process to improve LCDU and LER/LWR; in this case, the ASD is used as a corrective step.

To develop an ASD process that is relevant to device manufacturing, we only consider the gases present on a plasma etch chamber as precursors for ASD. We utilize the plasma assistance of the etch chamber to develop an ASD process by Plasma enhanced chemical vapor deposition, rather than by the more commonly exploited atomic layer deposition. This is more challenging since radicals from precursor dissociation are known to be highly reactive on the surface. However, it was recently demonstrated the selective PECVD of a silicon film on SiON surfaces using SiF4/H2 plasma[3].

In this presentation, we will demonstrate ASD by PECVD on SnOx (a EUV resist material) vs SiO-based materials (underlayer) in a 300 mm plasma etch tool, and the impact of plasma precursors and parameters on selectivity. We will show that we can selectively deposit film on SnOx. Results on full wafers and patterned samples will be presented. Thanks to the use of an in-situ plasma diagnostic, such as optical emission spectroscopy, as well as of ex-situ surface diagnostics such as X-ray photoelectron spectroscopy and scanning electron microscopy, we will discuss the mechanisms inherent to the selective growth and discuss the impact of chemistry of neighboring materials and pattern density.

1 J.Church, “Plasma based ASD for EUV resist defectivity reduction and process window Improvement” *AVS* (2021) Nov 2020

2 B. Vincent et al, Proc. *SPIE 11323,* “Extreme Ultraviolet (EUV) Lithography XI,”1132326 (23 Mar 2020)

3 G. Akiki et al, “Origin of area selective plasma enhanced chemical vapor deposition of microcrystalline silicon,” *J. Vac. Sci Technol.A* 39 (2021) 013201

9:20am **AP+2D+AS+EM+PS+SS+TF-MoM-4 Impact of Post-Exposure Treatments on TMSDMA-Passivated SiO_2 Surfaces*, Anthony Valenti*,** *C. Vallée, C. Ventrice,* SUNY Polytechnic Institute, Albany*; K. Tapily, K. Yu, S. Consiglio, C. Wajda, R. Clark, G. Leusink,* TEL Technology Center, America, LLC

As the scale of semiconductor devices continues to shrink, conventional approaches to fabrication such as photolithographic patterning are becoming limited in their ability to provide the precision and resolution required for smaller and smaller features. Over the last several years, a bottom-up and self-aligned patterning technique known as area-selective deposition (ASD) has been explored. With this technique, the deposition process is manipulated in such a way as to only promote growth on one type of surface on a patterned substrate. This is typically achieved by inhibiting specific surfaces through the selective chemisorption of molecules that are inert to the reactants used for growth of the material of interest. Aminosilane precursors such as *N*-(trimethylsilyl)dimethylamine (TMSDMA) are of recent interest due to their potential use in area-selective atomic layer deposition (AS-ALD). With their strong selective chemisorption on SiO_2 surfaces versus Si and non-oxidized metal surfaces, these precursors can be used to block deposition of metals on SiO_2 while not inhibiting growth on Si or metal surfaces. For aminosilanes to be used as inhibiting precursors in AS-ALD, the resulting layer must maintain its passivation throughout a dozen or more ALD cycles. This study investigates the impact of various common ALD co-reactant/post-exposure treatments on SiO_2 surfaces passivated via exposure to TMSDMA, including ozone exposure, H_2 plasma treatment, and H_2 plasma treatment followed by H_2O vapor exposure. This project also explores using a second inhibitor dosing via NF_3 plasma treatment in order to fluorinate any nucleation sites left vacant on the SiO_2 surface after TMSDMA exposure. These treatments were conducted on samples of TMSDMA adsorbed on Si(100) substrates with 1000 Å thick thermal oxide surfaces. Water contact angle measurements were taken of each sample to determine relative surface passivation of each sample and to monitor temporal degradation of the surfaces over a timescale spanning weeks. Angle-resolved X-ray photoelectron spectroscopy and attenuated total reflection/Fourier transform infrared spectroscopy were performed in order to determine the chemical state of each surface. Temperature programmed desorption measurements were conducted to assess the relative coverage of the inhibiting film on each sample and their stability at higher temperatures.

9:40am **AP+2D+AS+EM+PS+SS+TF-MoM-5 Area-Selective ALD Using Small Molecule Inhibitors of Different Sizes: Single and Sequential Inhibitor Dosing***, **Pengmei Yu**, M. Merkx, I. Tezsevin,* Eindhoven University of Technology, Netherlands*; P. Lemaire, D. Hausmann,* Lam Research Corp.*; T. Sandoval,* Federico Santa María Technical University, Chile*; W. Kessels, A. Mackus,* Eindhoven University of Technology, Netherlands

Due to the continuous scaling of semiconductor device features, area-selective atomic layer deposition (ALD) is gaining attention for enabling bottom-up fabrication with atomic-scale control. Area-selective ALD can be achieved by surface deactivation of the non-growth area using inhibitor molecules. Small molecule inhibitors (SMIs) are of great interest due to the vapor-phase application and corresponding industrial compatibility.[1] Our previous work established that SMIs block precursor adsorption by a combination of chemical passivation of surface sites and steric shielding.[2] In this contribution, we compared three SMIs of different sizes for SiO_2 inhibition on the Al_2O_3 surface, namely acetic acid (HAc), acetylacetone (Hacac), and 2,2,6,6-tetramethyl-3,5-heptanedione (Hthd), and explored sequential dosing of two different SMIs to increase the overall inhibitor packing.

We first focused on the use of a single SMI and studied how the size influences their performance. By in-situ spectroscopic ellipsometry and infrared spectroscopy studies, it is observed that using either a smaller (HAc) or a larger (Hthd) SMI than Hacac[3] could improve SiO_2 ALD inhibition. Density functional theory and random sequential adsorption simulations were performed to further understand experimental findings. We found that although both steric shielding and chemical passivation are required for effective precursor blocking by SMIs, neither of them plays a dominating role. As compared to Hacac, HAc performs better due to its small size, yielding denser packing and thereby a higher degree of chemical passivation. Hthd on the other hand, benefits from its bulkiness, resulting in a higher contribution from steric shielding.

In an effort to achieve a higher selectivity, we explored whether sequentially dosing of two different SMIs can lead to higher surface coverage and deactivation. It is found that enhanced precursor blocking of 98.4 ± 0.2 % could be achieved by dosing HAc and Hthd sequentially, which is higher than either 96.0 ± 0.6 % by Hthd or 97.0 ± 0.5 %by HAc solely. Results for various combinations of inhibitors and sequences will be presented.

In summary, this work illustrates that varying the size of SMIs could bring benefits from either higher steric shielding or chemical passivation components for improved precursor blocking performance. In addition, it is demonstrated that combination of SMIs could potentially be an effective strategy for achieving higher selectivity.

[1] A.J.M. Mackus *et al.*, Chem. Mater. 31, 2 (2019).

[2] M.J.M. Merkx *et al.*, J. Phys. Chem. C 126, 4845 (2022).

[3] M.J.M. Merkx *et al.*, J. Vac. Sci. Technol. A 39, 012402 (2021).

10:00am **AP+2D+AS+EM+PS+SS+TF-MoM-6 Role of Catalytic Surface Reactions During Area-Selective Tan ALD for Precursor Blocking Using Aniline Molecules***, **Marc Merkx**[1], I. Tezsevin, P. Yu, R. Heinemans, R. Lengers, E. Kessels, A. Mackus,* Eindhoven University of Technology, Netherlands*; T. Sandoval,* Federico Santa Maria Technical University, Chile

The semiconductor industry is running into significant issues regarding RC-delays in state-of-the-art interconnect structures. A solution is to selectively deposit the transition metal nitride diffusion barrier on the dielectric via sidewalls but not at the bottom, known as a bottomless barrier structure.[1]. In this contribution, area-selective TaN ALD is investigated using aniline as a small molecule inhibitor (SMI),[2] with the focus on studying the catalytic surface reactions that take place on the metal non-growth area after aniline adsorption.

Area-selective TaN ALD was achieved using a three-step (i.e. ABC-type) ALD cycle using: (A) aniline as SMI, (B) tert-butylimidotris(dimethylamino)tantalum (TBTDMT) as the precursor molecule, and (C) an Ar-H_2 plasma as the co-reactant. This process was found to selectively deposit TaN on dielectric surfaces (e.g. Al_2O_3 and SiO_2) considering the metal surfaces (e.g. Co, Ru) as non-growth area. It was observed that the selectivity of the process is strongly dependent on the employed substrate temperature. At 175 °C only ~1 nm TaN can be deposited selectively, whereas by raising the substrate temperature to 300 °C ~3 nm of selective TaN growth was achieved on Al_2O_3, with respect to Ru as the non-growth area.

An explanation for the strong temperature dependence for the selectivity of this process could be the catalytic reactivity of the metal non-growth area. For example, through density functional theory (DFT) calculations, it was found that aniline can undergo a hydrogenolysis reaction on transition metal surfaces, where the amine group splits off as NH_3 while benzene remains adsorbed on the surface. This reaction eliminates the NH_2 groups from the surface that could otherwise interact with incoming precursor molecules.[3] Experimental and simulation results will be presented to provide insight into the role that catalytic surface reactions play during area-selective ALD on metal surfaces.

[1] Merkx et al., Atomic Limits **7**, (2022) https://www.atomiclimits.com/2022/04/18/

[2] Merkx et al., Chem. Matter **32**, 7788-7795 (2020)

[3] Merkx et al., Chem. Matter. **32**, 3335-3345 (2020).

10:40am **AP+2D+AS+EM+PS+SS+TF-MoM-8 AVS Russell and Sigurd Varian Awardee Talk: Sequential Application of Two Inhibitors to Achieve Area-Selective Atomic Layer Deposition of Dielectric on Metal***, **Tzu-Ling Liu**[2][3], M. Harake, S. Bent,* Stanford University

Area-selective atomic layer deposition (AS-ALD), which provides a bottom-up approach to fabricate patterned structures, has been considered as a prospective solution to overcome the challenges in current semiconductor manufacturing processes. To enable more applications of AS-ALD, it is critical to expand the AS-ALD toolbox to different types of surfaces. Previous studies have successfully demonstrated selective deposition of dielectrics on the dielectric (DoD) regions of metal/dielectric patterns using alkanethiols and phosphonic acids as the inhibitors for metal surfaces. However, doing the reverse pattern transfer, i.e., selective deposition of dielectrics on the metal (DoM) regions, is less well-investigated because selective inhibitor deposition on dielectric over metal is more challenging. Taking organosilane, a common inhibitor choice for dielectric surfaces, as an example, it can also adsorb on metal substrates when native metal oxide is present. Hence, it is important to develop a strategy to protect metal surfaces from the adsorption of organosilane inhibitors for achieving AS-ALD of DoM.

In this work, we demonstrate a two-step strategy to achieve selective deposition of DoM by using two different SAMs with orthogonal surface chemistry, i.e., one SAM preferentially adsorbs on the metal, which serves as a protector to prevent the adsorption of the other SAM onto the metal, and the other primarily adsorbs on the dielectric, which serves as an inhibitor for AS-ALD. We sequentially perform dodecanethiol (DDT) deposition on Cu surfaces, followed by octadecyltrimethoxysilane (OTMS) deposition on SiO_2 surfaces. Since the Cu surfaces are protected by DDT in the first step, OTMS selectively forms a well-packed self-assembled monolayer (SAM) only on SiO_2. With this strategy, we demonstrate AS-ALD of ZnO and Al_2O_3 on Cu (growth surface) over SiO_2 (non-growth surface)

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[1] **2021 TFD James Harper Awardee**

[2] **TFD James Harper Award Finalist**

[3] **AVS Russell and Sigurd Varian Awardee**

after applying a thermal step to selectively remove DDT protector from Cu. The blocking results show that selectivity > 0.9 can be maintained after 35 cycles of ZnO ALD (corresponding to 5.6 nm of ZnO on a reference native SiO_2-covered Si substrate) and 15 cycles of Al_2O_3 ALD (corresponding to 1.4 nm of Al_2O_3), respectively, using this sequential two-step SAM process. Our study helps expand the selective deposition toolbox and provide more possible applications for AS-ALD in next generation electronic devices.

11:00am **AP+2D+AS+EM+PS+SS+TF-MoM-9 Carborane Self-Assembled Monolayers for Area-Selective Deposition***, Michelle Paquette, R. Bale, R. Thapa, S. Pinnepalli,* University of Missouri-Kansas City*; J. Bielefeld, S. King,* Intel Corporation

Area-selective deposition (ASD) is an important strategy in improving the fidelity of and/or reducing the complexity of current multi-pattern pitch-division processes. An expanded palette of ASD materials and processes is needed. Boron carbide (BC) has been demonstrated to be a compelling candidate for low-*k* dielectric, etch stop, diffusion barrier, and patterning-assist layers, due to its robust electrical, mechanical, and chemical properties, as well as unique etch chemistry. The molecular carborane precursor is of interest for BC-based self-assembled monolayers (SAMs). This is a symmetric twelve-vertex molecule, with many available and typically sublimable derivatives. For SAM applications, carborane stands out in that its 3D symmetry allows for the formation of well-ordered layers, and the termination of its vertices by labile H atoms allows for cross-linking with a variety of mechanisms including heat, plasma, and radiation (e.g., UV, e-beam). Carborane SAMs can conceivably fulfill various roles in ASD schemes, including as an intrinsically selective functional dielectric layer (e.g., diffusion barrier), sacrificial layer (e.g., hard mask), direct-writeable layer, or blocking layer to facilitate the selective deposition of other materials. We describe progress in the deposition and characterization of carborane SAMs toward the development of a range of ASD schemes and applications.

11:20am **AP+2D+AS+EM+PS+SS+TF-MoM-10 Peter Mark Memorial Award Talk: Reactive Inhibitory Chemistries for Area Selective Depositions and Their Application in Back End of the Line Processes***, **Rudy Wojtecki**[1],* IBM Almaden Research Center **INVITED**

Area selective depositions (ASD) describe self-aligned processes where the chemical contrast of surfaces are exploited to selectively grow a film. ASD can be applied to a variety of fabrication schemes to improve tolerance to overlay errors in fully aligned via schemes or achieve device performance improvements by reduce resistance between interconnect levels in barrier-less contacts that reduce stage delay. While ASD processes are accessible through a variety of methods – differences in surface reactivities between materials, self-assembled monolayers (SAMs) and small molecule inhibitors, to name a few – reactive organic inhibitors and their application in ASD processes will be described. Reactive inhibitor compositions can be selectively deposited on a metal portion of a pre-pattern surface, then undergo (i) a crosslinking reaction or (ii) further chemical transformations used to grow an inhibitory film to a desired thickness. Crosslinking of a monolayer film for ASD was demonstrated with the introduction of diyne moieties into a SAM composition, which is crosslinked under either UV or thermal treatment. These crosslinked monolayers were found to enhance selectivity in an ASD process and reduce defects on patterned substrates. With synthetic modifications to increase the length of the SAM, further reductions in defectivity was achieved as well as the ASD of TaN. Electron beam irradiation of aliphatic moieties are also known induce crosslinking. With the use of hydroxamic acid head groups the chemical contrast between exposed (crosslinked) and non-exposed regions could be significant enough to enable a patternable ASD process where, as the crosslink density increased the selectivity of the monolayer is further improved. These SAM chemistries require solution-based coating methods but the concept of a crosslinkable inhibitor could also be translated to a vapor phase process, demonstrated with propargyl amine and vinyl pyridine. To tailor inhibitor thickness in strategy (ii) chemically reactive surfaces were exploited where monomers are selectively attached to a metal surface then polymers grown in an area selective manner with tailorable thicknesses, demonstrated with a polynorbornene and poly(vinylpyridine). This tailorable thickness presents several advantages over monolayers – such as enabling ASD on patterns with topography (sharp corners & bends) or the control of lateral overgrowth. These reactive inhibitory chemistries demonstrate an inhibitory chemistry strategy for ASD and their use in back end of the line applications such as fully aligned via, barrier-less contacts or zero-line end extensions.

Applied Surface Science Division
Room 320 - Session AS+LS+RE+SS-MoM

Probing Surface and Interface Structure with X-ray Photoelectron Spectroscopy: In Memory of Charles Fadley

Moderators: Gregory Herman, Oregon State University, **Theva Thevuthasan**, Pacific Northwest National Laboratory

9:00am **AS+LS+RE+SS-MoM-3 X-Ray Spectroscopic Identification of Strain and Structure-Based Resonances in a Series of Saturated Carbon-Cage Molecules: Adamantane, Twistane, Octahedrane, and Cubane***, **Trevor Willey**, J. Lee,* Lawrence Livermore National Laboratory*; D. Brehmer, O. Paredes Mellone,* SLAC National Accelerator Laboratory*; L. Landt,* Lawrence Livermore National Laboratory*; P. Schreiner, A. Fokin, B. Tkachenko,* Institute of Organic Chemistry, Justus Liebig University, Germany*; A. de Meijere, S. Kozhushkov,* Institute for Organic and Biomolecular Chemistry, Georg-August-University, Germany*; T. van Buuren,* Lawrence Livermore National Laboratory

Novel nanocarbons such as fullerenes, nanotubes, graphene, and nanodiamond reside at the cutting edge of nanoscience and technology. Along with chemical functionalization, geometrical constraints (such as extreme curvature in nanotubes, or defects within or at the surfaces of diamond nanoparticles) significantly alter the electronic states of the nanocarbon material. Understanding the effects of steric strain on electronic structure is critical to developing nanoelectronic applications based on these materials. This paper presents a fundamental study of how strain affects electronic structure in a benchmark series of some fundamental saturated carbon cage compounds. Adamantane, C10H16, the smallest diamondoid, and arguably the smallest nanodiamond crystallite, has carbon atoms essentially commensurate with diamond lattice positions and possesses by far the least bond strain of this series. Twistane also is a C10H16 isomer but the fixed cyclohexane twist conformation of the central ring introduces some strain into the cage. Octahedrane, (CH)12, and cubane, (CH)8, are considerably much more strained, culminating in cubane where carbon-carbon bonds lie either parallel, or orthogonal to one another. Using gas-phase near-edge X-ray absorption fine structure (NEXAFS) spectroscopy to probe the unoccupied electronic states, we observe two major progressions across this series. First, a broad C–C σ* resonance in the absorption splits into two more narrow and intense resonances with increasing strain. Second, the first manifold of states previously associated with tertiary C-H σ* in the diamondoid series appears to broaden and shift to lower energy. This feature is more than twice as intense in cubane as in octadedrane, even though these two molecules have only tertiary carbons, with chemical formula (CH)x. The spectral differences are entirely due to the shape of the molecules; in particular, in cubane, the features arise from a high degree of p-p interaction between parallel C-C bonds. In contrast to the conventional wisdom that near-edge X-ray absorption is primarily an atomically localized spectroscopy, molecular shape and associated bond strain lead to the dominant features in spectra acquired from this fundamental series of carbon cage structures.

9:20am **AS+LS+RE+SS-MoM-4 Composition and Thermal Stability Analysis of Passive Films on NiCr and NiCrMo Alloys***, **Keithen Orson**, A. Costine, E. Romanovskaia, J. Scully, P. Reinke,* University of Virginia

Ni-Cr based super-alloys are important because of their corrosion resistance, which derives mainly from a thin passive layer of chromia (Cr_2O_3). During aqueous corrosion, a complex surface layer containing $Ni(OH)_2$, $Cr(OH)_3$, and Cr_2O_3 forms whose chemistry and structure are still subject of discussion. Our work is designed to study how non-equilibrium growth of the passive layer during aqueous corrosion affects the properties of the passive layer. We apply a range of electrochemical conditions to two alloys - Ni22wt%Cr, and Ni22wt%Cr6%Mo. Alloys are processed in pH 4 aqueous chloride solution. The electrochemical reaction step uses high or low current density (100-0.1 nA/cm^2) to achieve fast and slow passive layer growth that is far or near equilibrium, respectively. The second step was a 10 ks potentiostatic hold at +0.2V. Electrochemical processing was followed Angle-Resolved X-Ray Photoelectron Spectroscopy (ARXPS) analysis to characterize the oxide and hydroxide chemistry of the passive layer and underlying alloy. Annealing to 400 °C served as a proxy to assess the passive layers stability, which we propose is related hydroxide network connectivity and pitting resistance. In as-prepared samples, Ni and Cr hydroxides are dominant in the passive layer, while chromia and $Cr(OH)_3$ are the dominant species at elevated temperatures. The underlying alloy tends to be moderately enriched in Cr. Under all conditions and temperatures, Cr is present as a mix of oxide and hydroxide with the oxide

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[1] **Peter Mark Memorial Award Winner**

dominating at higher temperatures. In contrast, $Ni(OH)_2$ is detected at low temperatures, but no NiO is observed. For molybdenum-containing alloys, MoO_x and Cr_2O_3 coexist until MoO_x is reduced at T>300˚C. Continuous XPS spectra taken during annealing indicate smooth transitions between hydroxide and oxide visible in the O1s and C2p3/2 peak shape, while for Mo 3d3/2 and Ni2p3/2 peaks narrow transition regions for reduction are identified. Oxide thickness decreases with increasing temperature due to oxide loss from reduction and volatilization. The fast and slow growth on Mo-containing alloys without a subsequent potentiostatic hold produced a marked difference in oxide thickness. Molybdenum content affects multiple characteristics of the passive layer, including thickness, layering, and chromia content. Our work demonstrates how differing preparation conditions affect the chemistry and layering of NiCr and NiCrMo alloys. These results will be interpreted in the context of passive film performance and can ultimately be used to design alloys for optimal corrosion resistance.

9:40am **AS+LS+RE+SS-MoM-5 Reversible Changes in Surface Charging and Surface Oxide of $NiFe_2O_4$ Thin Films: A Temperature Dependent X-Ray Photoemission Study**, ***Arjun Subedi***, *D. Yang, X. Xu, P. Dowben,* University of Nebraska-Lincoln

We have observed large binding energy shifts in temperature dependent X-ray photoelectron spectroscopy (XPS) of the $2p_{3/2}$ core levels of both Ni and Fe atoms in nickel ferrite ($NiFe_2O_4$) thin films grown on Al_2O_3. The binding energies of the core levels were found to be sensitive to photovoltaic charging. The apparent binding energies decreased by more than 5 eV for both core levels when the temperature was increased to 510 K from room temperature. This is evidence of large surface charging of the sample and indicative of insulating behavior at lower temperatures. The XPS spectra at higher temperatures were observed to be different from that at lower temperatures, suggesting a different surface oxide at higher temperatures. When temperature was lowered from 510 K to room temperature, the changes in surface charging and nature of the surface oxide were reversible. We conclude that the nature of the surface oxide is temperature dependent.

10:00am **AS+LS+RE+SS-MoM-6 The Reproducibility Crisis in Science as Manifested in X-Ray Photoelectron Spectroscopy (XPS). What's Been Done, and What's Being Done About It?**, ***Matthew Linford,*** Brigham Young University*; D. Baer,* PNNL*; G. Major,* Brigham Young University

X-ray photoelectron spectroscopy (XPS) is the most important method for chemically analyzing surfaces. Conventional XPS probes 5 - 10 nm into surfaces, revealing both the atomic compositions and chemical states of the atoms at surfaces. During the past few decades, there has been a significant increase in the use of XPS worldwide, both in the number of papers published that show XPS data and in the number of new XPS systems being sold. However, the world appears to have created new XPS instruments faster than XPS experts. Indeed, a recent paper suggested that about 40% of the XPS peak fitting reported in the scientific literature is deeply flawed (see *J. Vac. Sci. Technol. A***2020**, *38*, 061204). An anecdotal report suggests that the XPS peak fitting in submitted manuscripts is even worse. In this talk, we discuss some of the efforts that are being made to address the reproducibility crisis in science vis-a-vis XPS and surface analysis in general. These efforts include a collection of guides on XPS that was recently published in JVST, a second set of guides to JVST that is currently accepting submissions, a set of guides being written to Applied Surface Science Advances that is also currently accepting submissions, and 'XPS Insight Notes' that will be accepted by Surface and Interface Analysis. These latest two sets of guides will accept papers on any surface analytical technique. It is hoped that by providing useful guidance on XPS and other surface analytical methods, these efforts will improve the quality of data collection and analysis that is appearing in the surface literature. This talk will also discuss common errors in XPS peak fitting in the literature and ways to fix them.

10:40am **AS+LS+RE+SS-MoM-8 Study of Surface Oxides on $Pt_3Ni(111)$ and $Pt_3Co(111)$ using Ambient Pressure XPS**, ***Bongjin Simon Mun,*** Gwangju Institute of Science and Technology, Republic of Korea **INVITED**

Utilizing AP-XPS, the surface chemical states of $Pt_3Ni(111)$ and $Pt_3Co(111)$ is examined under CO oxidation condition. Under elevated oxygen pressure, the presence of surface segregation of transition metals is clearly observed in AP-XPS. Also, with AP-STM, the formations of nanostructured transition-metal oxides are confirmed during the segregation. As CO oxidation occurs, the interfacial oxygens on the nanostructured metal oxides display unique chemical reactivity. Difference between Pt_3Ni and Pt_3Co alloys surface will be presented.

11:20am **AS+LS+RE+SS-MoM-10 Probing the Oxidation Chemistry of TRISO Nuclear Fuels Using Depth Profiled XPS and Ambient Pressure XPS**, ***Jeff Terry***, Illinois Institute of Technology

While the use of TRISO fuels has been long postulated within High Temperature Gas Reactors, an additional use is possible as an accident tolerant fuel in Light Water Reactors (LWRs). Before TRISO fuels can be used in LWRs, the corrosion properties of the different layers of TRISO fuels must be well understood. Photoelectron Spectroscopy (PES) has long been utilized to study the oxidation behavior of materials due to its sensitivity to both element and chemical state. The problem with (PES) has been that it has historically been an technique that required Ultrahigh Vacuum conditions for measurements. This made it difficult to study corrosion in situ. New instruments have expanded the capabilities of PES. It is now possible to measure photoemission spectra at ambient pressure. We have measured the in situ corrosion of a SiC layer grown as a TRISO simulant at a pressure of 1 mbar of H_2O at temperatures of 500 C using an ambient pressure photoemission system. In addition, we have grown multilayer SiC/ZrN/C systems designed to protect the environment from silver release. We will report on the corrosion chemistry of the SiC, ZrN, and C layers as measured using ambient pressure photoemission. Finally, We can also compare this to samples oxidized under high pressures of water and then measured with sputter-depth profiled conventional XPS measurements. These measurements help us to understand the potential failure modes of accident tolerant nuclear fuels.

11:40am **AS+LS+RE+SS-MoM-11 Environmental X-ray Photoelectron Spectroscopy Study of Catalyst-Ionomer Interactions in Polymer Electrolyte Membrane Fuel Cells**, ***Jayson Foster***, *S. Zaccarine, M. Dzara,* Colorado School of Mines, USA*; C. Baez-Cotto,* National Renewable Energy Laboratory*; S. Kim,* Colorado School of Mines, USA*; M. Batool, J. Jankovic,* University of Connecticut*; M. Ulsh, S. Mauger,* National Renewable Energy Laboratory*; S. Pylypenko,* Colorado School of Mines, USA

Proton exchange membrane fuel cells (PEMFCs) are an important technology providing on-demand energy without contributing to greenhouse gases. High demand for this technology requires scaled-up fabrication of PEMFC catalyst layers (CLs), thus motivating studies that relate catalyst chemistry and morphology to processing parameters and performance characteristics. Currently, interfacial interactions between catalyst and ionomer are not well understood fundamentally, including the evolution of this interface under humidified conditions.

Environmental X-ray photoelectron spectroscopy (EXPS) is a highly surface-sensitive technique primed to provide information into the surface properties of CLs and further improve understanding of interfacial interactions among the catalyst, support, and ionomer. Although Nafion ionomer is inherently susceptible to X-ray degradation, XPS can be used effectively through a modified acquisition strategy developed previously in our group. In this work, EXPS was used to probe CLs using a series of electrodes prepared by a Mayer rod coating method. The catalyst-ionomer interface was investigated as a function of carbon support material, loading of the Pt catalyst on the support, and ionomer content in the catalyst ink. Surface information was acquired using *ex situ* and *in situ* XPS to emphasize this technique's capabilities at probing ionomer interactions and their evolution in a humidified environment. Scanning transmission electron microscopy (STEM) was used to visualize distribution of Pt nanoparticles on support, relating catalyst and support properties to their surface behavior while integrated with ionomer. Furthermore, scanning electron microscopy (SEM) and STEM imaging in combination with energy-dispersive X-ray spectroscopy (EDS) mapping of electrode cross-sections were utilized to visualize distribution of ionomer and Pt in the CL to further assist with interpretation of EXPS data. Results from this dataset emphasize the strength of this technique to study complex interfaces in PEM catalyst layers motivating further work expanding to other catalysts and ionomers.

Biomaterial Interfaces Division
Room 318 - Session BI+AS+PS-MoM

Biomolecular Interfaces and Underwater Adhesion

Moderator: Morgan Alexander, University of Nottingham, UK

8:20am **BI+AS+PS-MoM-1 Supported Lipid Bilayers as Model Systems to Understand Molecular Interactions at Complex Solid/Liquid Interfaces***,* ***Pierluigi Bilotto,*** Centre for Electrochemistry and Surface Technology, Austria*; L. Mears, M. Valtiner,* Vienna University of Technology, Austria

Generating a detailed molecular understanding of complex, simultaneous inter actions at reactive and/or dynamic solid|fluid interfaces is a challenge across disciplines, and has intrigued researchers for decades.[1, 2] Whether it is, for example, in medical adhesives, friction of articular cartilage,[3] or the adhesion of organisms in seawater,[2] complex macroscopic properties at crowded biologic solid|liquid interfaces are mediated by large numbers of individual nanoscale interactions.[4] Exactly this complex competition and molecular structuring at interfaces are central to a multitude of interfacial phenomena, such as membrane transport,[5] membrane conductance, [6,7] cellular adhesion [8] and adhesion regulation in the marine environment. [9]

In our previous works, we characterised a lipid-based model system (LMS) in terms of its stability and bending properties by employing atomic force microscopy and surface forces apparatus. [10] Then, we further modified its outer face with amine-terminating polymers to investigate the specific electrostatic interaction between the amine and a negatively charged mica surface. Then, we examined how interaction forces are affected by the electrolyte concentration, funding a direct exponential like decay between adhesion and electrolyte concentration. Specifically, we found a decrement of 90% in adhesion in a 1M sodium chloride environment. These fundings suggested the presence of a competing mechanism which was confirmed by a kinetic model at the interface involving two competing Langmuir isotherms. Finally, we could estimate ion/surface interaction energies from the experimentally recorded interaction force measurements.[11]

In the talk we will discuss these works and present the new research opportunities coming out from these results.

(1) Israelachvili, J.; Wennerstr̈om, H. Nature 1996, 379, 219–225

(2) Stock, P. *et al,* ACS Nano 2017, 11, 2586–2597

(3) Shoaib, T. *et al,* Biomater. Sci. 2020, 8, 3944–3955

(4) Cai, L. *et al,* ACS Nano 2017, 11, PMID: 28383885, 3727–3732

(5) Gage, P. W.; Quastel, D. M. J. The Journal of Physiology 1966, 185, 95–123

(6) Stieve, H.; Bruns *et al* Zeitschrift f̈ur Naturforschung C 1978, 33, 574–579

(7) Stieve, H.; Pflaum *et al,* Zeitschrift f̈ur Naturforschung C 1985, 40, 278–291

(8) Ohgaki, M. *et al,* Journal of Biomedical Materials Research 2001, 57, 366–373

(9) He, X.; *et al,*Colloids and Surfaces B: Biointerfaces 2016, 146, 289–295

(10) Bilotto, P.; Lengauer, M.; *et al* Langmuir 2019, 35, 15552–15563

(11) Bilotto, P *et al* ACS Physical Chemistry Au 2021, 1, 45-53

8:40am **BI+AS+PS-MoM-2 Recombinant Lubricin Improves Anti-Adhesive, Wear Protection and Lubrication of Collagen II Surface***, H. Yuan,* Tianjin University, China*;* ***Laura Mears,*** Vienna University of Technology, Austria*; R. Su,* Tianjin University, China*; M. Valtiner,* Vienna University of Technology, Austria

Lubrication in articular joints is regulated by a number of biomolecules including the collagen of the cartilage, lubricin and lipids in the synovial fluid. Camptodactyly-arthropathy-coxa vara-pericarditis syndrome (CACP) is a joint disease, which causes a lack of lubricin, leading to failed lubrication as well as abnormal deposition at cartilage surfaces. Injection of recombinant lubricin (R-LUB) is a promising way to treat the disease. Here, the protein adsorption and lubrication behavior of type II collagen (COL II), mimicking the cartilage surface, upon R-LUB injection were followed by a surface plasmon resonance spectroscopy and surface forces apparatus. The results indicated R-LUB can bind well on COL II surface and the layer of COL II/R-LUB complex exhibited a much lower nonspecific adsorption of BSA (3.25 ng/cm^2) and LYS (0.26 ng/cm^2) compared to those of the COL II layer (32.7 ng/cm^2, 7.26 ng/cm^2), respectively. Normal force measurement demonstrated there were repulsive forces between the COL II/R-LUB complex and different surfaces with $-COO^-$, $-NH_3^+$ and $-CH_3$ groups. Likewise, COL II had a high coefficient of friction (μ~0.48) with surface damage at 2 μm/s and wear pressure of 1.56 MPa. In contrast, the coefficient of friction of COL II/R-LUB complex was dramatically decreased to ∼0.014-0.13 with surface damage at 13 μm/s, the complex even shows an ultralow coefficient of friction of 0.008 at the lowest loading <3 mN. Furthermore, R-LUB modification boosts the strength of the surface against abrasive wear (damage) of 11.96 MPa, which was 7.7 times higher than that of COL II alone. Hence, R-LUB may act as an anti-adhesive and lubrication layer adsorbed on COL II surfaces to develop strong steric-repulsive interactions and lubrication to prevent direct surface contact. Our results provide fundamental insights into the adsorption and lubrication behavior for understanding biological lubrication, especially using R-LUB for CACP disease treatment.

9:40am **BI+AS+PS-MoM-5 Hyaluronic Acid-Dopamine Conjugate for Facile Deposition onto Collagen I with Enhancing Anti-Adhesion and Lubrication***, H. Yuan,* Tianjin University, China*; L. Mears, M. Valtiner,* Vienna University of Technology, Austria*;* ***Rongxin Su,*** Tianjin University, China

Collagen I matrix (COL I) has been applied clinically for repairing damaged cartilage, but it has poor protein resistance and insufficient lubrication performance, which seriously affects the repairing performance for cartilage. Hyaluronic acid (HA) has good anti-adhesive and lubrication properties, and seems to be a potential candidate to improve treatment with COL I, but it cannot be immobilized onto the collagen surface. Inspired by mussels, dopamine (DA) was chemically grafted to HA to form the HADA conjugate, which could firmly adhere to the surface of COL I by dopamine oxidation and reacted with amine from COL I. The protein resistance and lubrication properties of COL I and HADA-modified COL I (COL I/HADA) surfaces were followed by quartz crystal microbalance with dissipation and surface force apparatus techniques. The optimal modified time of HADA on COL I surface was 8 h. The nonspecific adsorption of bovine serum albumin (BSA) and lysozyme on COL I/HADA were reduced to 1/25 and 1/42 of that on COL I. COL/HADA also displayed very good resistant to high concentrations of BSA. Upon HADA modification, the interaction force between COL I and the surfaces with positive and negative charges sharply decreased from 2-6 mN/m to 0, demonstrating that the COL I/HADA surface had a strong anti-adhesion property. The coefficient of friction of COL I (∼0.65) was quite high displaying poor lubricating ability, while that of COL I/HADA reduced to ∼0.16. Upon HADA modification, the wear occurred at a shear rate of 14 μm/s, and the surface resistance to abrasive wear (damage) was greatly improved to 9.7 MPa, about 12 times higher than the COL I surface. These results indicated that HADA-modified COL I is a promising anti-adhesive and lubricating joint repair material, especially in the field of osteoarthritis treatment.

10:00am **BI+AS+PS-MoM-6 Anti-Fouling Properties of Amphiphilic Zwitterionic Hydrogels***,* ***Lisa Schardt,*** Ruhr University Bochum, Germany*; A. Martínez Guajardo,* University of Potsdam, Germany*; J. Koc,* Ruhr University Bochum, Germany*; J. Clarke, J. Finlay, A. Clare,* Newcastle University, UK*; H. Gardner, G. Swain, K. Hunsucker,* Florida Institute of Technology*; A. Laschewsky,* University of Potsdam, Germany*; A. Rosenhahn,* Ruhr University Bochum, Germany

Hydrogels exhibit excellent biocompatibility and resistance against nonspecific attachment of organisms most likely due to their stable hydration shell.[1] Zwitterionic polymers like the sulfobetaine N-(2-methacryloxy)-ethyl-N,N-dimethylammoniopropansulfonate (SPE) are promising candidates foranti-fouling coatings. However, due to low mechanical strength, their performance in the field is limited.[2] N-butyl methacrylate (BMA) was added in amounts between 0 and 50% to copolymers containing SPE and the photocrosslinker 2-(4-benzoylphenoxy)ethyl methacrylate (BPEMA) to tune the hydrophilicity of the resulting hydrogel properties. The rearrangement of the polymer upon immersion in seawater was characterized by under-water contact angle goniometry. The swelling and resistance against mineral particles were measured with surface plasmon resonance (SPR) and sediment immersion tests. Biological anti-fouling experiments were performed using *Ulva linza* and field tests. Upon immersion in saltwater, the polymer chains rearranged to form hydrophilic surfaces and the degree of swelling depended on the salt concentration. The incorporation of BMA successfully altered the mechanical properties of the coatings resulting in a lower silt uptake. At the same time, the amphiphilicity did not hamper the anti-fouling performance in laboratory assays and a decrease of the settlement was observed in field tests.[3]

[1] A. Laschewsky, *Polymers*, **2014**, 6, 1544-1601.

[2] J. Koc, *Biofouling*, **2019**, 4, 454-462.

[3] L. Schardt, *Macromolecular Rapid Communications*, **2021**, 2100589.

10:40am **BI+AS+PS-MoM-8 Mussel Adhesion: A Fundamental Perspective on Factors Governing Strong Underwater Adhesion***, L. Mears, J. Appenroth, A. Celebi, A. Imre, H. Yuan,* TU Wien, Austria*; P. Bilotto,* CEST Centre for Electrochemistry and Surface Technology, Austria*; R. Su,* Tianjin University, China*;* ***Markus Valtiner,*** TU Wien, Austria

Tuning interfacial electrochemistry is central to the principle of the strong underwater adhesive of mussels. Here we critically discuss recent progress in the field, and we discuss how interfacial electrochemistry can vary interfacial forces by a concerted tuning of surface charging, hydration forces and tuning of the interfacial ion concentration. Mussel foot proteins contain a number of different functional groups, with much focus directed towards the catechol moiety. Therefore, we discuss some of our recent results in the area of adhesion of different functional groups in a saline environment. We also present new data from electrochemical surface force apparatus experiments that explore the difference in adhesion for oxidized and reduced forms of the catechol functional group against a mineral, mica, in different environments. These results raise interesting questions about the role of the catechol group. We propose new paths into understanding and utilizing redox-proteins and derived polymers for enhancing underwater adhesion in a complex salt environment.

11:00am **BI+AS+PS-MoM-9 Bioinspired Underwater Adhesives Using Amyloids from Commonplace Proteins***, M. Wilson,* NRC Post-doctoral Fellow sited at the Naval Research Laboratory, Chemistry Division*; M. Beasley,* NRC post-doc sited at the Naval Research Laboratory, Chemistry division*; K. Fears,* Naval research laboratory, Chemistry Division*; E. Yates,* US Naval Academy, Chemistry Department*;* ***Christopher So*** [1]*,* Naval Research Laboratory, Chemistry Division

Barnacles adhere permanently underwater using proteins that are delivered as a liquid, triggered to assemble, and cure as a bulk amyloid material in extreme seawater environments. More cosmopolitan than most other fouling organisms, barnacles rely on these materials to remain stuck at frigid ocean depths, as well as on hot intertidal coasts. We have previously been successful in designing sequences that can mimic the natural glue chemistry and structure, however bridging the gap between natural sequences and materials of practical use remains a challenge. Here, we mimic protein aggregation from the barnacle with unmodified food proteins as model systems and fabricate adhesives by curing them at the adhesive joint. We use temperature and time to control protein assembly and define the relationship between biophysical state and adhesive strength. Using thermal processing, we fabricate adhesives that approach the underwater lap shear strength of commercial marine and contemporary bioinspired chemistries. Though we observe differences in adhesive behavior between the examined proteins and their aggregation state, the presence of amyloids improves underwater performance across all proteins studied. We show that commonplace proteins can be delivered as a liquid, triggered to cure with chemistry or heat, and form strong underwater adhesives at the contact. The aggregation of commonplace proteins is therefore a viable pathway in creating strong underwater adhesives which, like the organisms that use them, can operate in extreme underwater conditions.

11:20am **BI+AS+PS-MoM-10 Incorporation of Antimicrobial Cyclic Peptides in Polymeric Materials***, D. Regan, Q. Lu, D. Barlow,* ***Kenan Fears,*** US Naval Research Laboratory

Polymeric coatings are used universally to protect structural materials and extend their operational lifetime. Microbial growth on these coatings, if unmitigated, present health risks and can diminish the protective performance of the coatings. For example, fungi have been linked to the degradation of aircraft surface coatings which can lead to corrosion of the underlying metals. After bans on heavy metal mixtures within surface treatments, a commercial void remains for a solution to prevent biodegradation of material surfaces. Building on the advancements within cyclic peptide synthesis, we test the antimicrobial activity of alpha and beta conformations of cyclic peptides against microorganisms of medical and industrial interest. Minimum inhibitory concentration (MIC) and microbial growth assays showed that cyclic peptides exhibited broad spectrum activity against gram-positive and gram-negative bacteria, yeasts, and algae. Furthermore, the cyclic peptides were mixed into a commercial polyester polyurethane coating, Irogran, and exposed to cultured isolates of biodegrading yeasts. For both cyclic peptide-Irogran blends, zero colony forming units were detected after a one-week exposure. These findings demonstrate how synthesized cyclic peptides retain their antimicrobial activity after incorporation into polymeric surface coatings to prevent the growth of problematic microorganisms.

11:40am **BI+AS+PS-MoM-11 Tuning Amphiphilicity of Alginic Acid-Based Polyelectrolyte Multilayers to Enhance Marine Fouling Resistance***,* ***Jana Karthäuser****, T. Gnanasampanthan, S. Spöllmann, R. Wanka, H. Becker, A. Rosenhahn,* Ruhr University Bochum, Germany

Polysaccharides are among other naturally occurring polymers commonly used in fouling-resistant coatings for both marine and medical applications. The anionic polysaccharide alginic acid (AA) is a non-toxic, eco-friendly, and readily accessible biopolymer that is widely used for biomedical purposes because of its high water-binding capacity. Thus, alginic acid is an interesting and promising building block to produce marine antifouling coatings. Unfortunately, in seawater, the biopolymer loses its antifouling efficacy due to the complexation of bivalent ions. An approach to overcome the susceptibility of charged polysaccharides, such as AA, is the blocking of the carboxylate groups by hydrophobic functional groups. The incorporation of amphiphilic moieties additionally changes the physicochemical properties of the coating and enables the tuning of fouling-resistant properties.[1]Layer-by-layer assembly of polyelectrolytes is a versatile and common technique to produce highly defined and reproducible coatings. The use of different or differently modified polyelectrolytes with opposite charges enables the charge-driven assembly.[2] To introduce amphiphilicity, different degrees of carboxyl groups of alginic acid were modified with pentafluoropropylamine. The influence of the amphiphilicity on the physicochemical characteristics of the modified alginic acid itself as well as of the coatings, when used alternately deposited with polyethyleneimine in multilayers, were investigated. Subsequently, the different degrees of modification of the AA-containing coatings with respect to the non-specific attachment of proteins by surface plasmon resonance spectroscopy and marine fouling organisms by attachment assays were examined in more detail and revealed an improved fouling resistance with increasing amphiphilicity.

1. Bauer, S. *et al.* Resistance of Amphiphilic Polysaccharides against Marine Fouling Organisms. *Biomacromolecules***17**, 897–904 (2016).

Gnanasampanthan, T. *et al.* Effect of Multilayer Termination on Nonspecific Protein Adsorption and Antifouling Activity of Alginate-Based Layer-by-Layer Coatings. *Langmuir***37**, 5950–5963 (2021).

Gnanasampanthan, T. *et al.* Amphiphilic Alginate-Based Layer-by-Layer Coatings Exhibiting Resistance against Nonspecific Protein Adsorption and Marine Biofouling. *ACS Appl. Mater. Interfaces***14**, 16062–16073 (2022)

MEMS and NEMS Technical Group
Room 302 - Session MN+AS+NS+QS+SE-MoM

Dynamics and Engineering of MEMS/NEMS

Moderators: Jürgen Brugger, EPFL, Switzerland, **Eva Weig**, University of Munich, Germany

9:00am **MN+AS+NS+QS+SE-MoM-3 MEMS-Based Surface Nanoengineering Using Thermal AFM Probes: 30 Years and Counting***,* ***Jürgen Brugger,*** École Polytechnique Fédérale de Lausanne, Switzerland **INVITED**

Soon after the first publication in 1985 of the atomic force microscope (AFM) attempts were made to extend AFM-based surface probing from microscopy to lithography [reviewed in 1]. The potential applications in writing and reading for data storagein the early years served as technology driver and showed remarkable performances [2]. One of the variants of AFM-based writing (and reading) operates a heated nano-tip to perform thermally induced phase changes of materials. The three-fold combination of nano-scale heat localization (30 nm scale), high temperature (~ 500 °C)and particularly fast heating/cooling cycles (10E-6 s) is unique and opens new opportunities for surface engineering and material conversion using heat.In the meantime, nano-tips and cantilevers were further perfected as nanotools to locally induce phase changes in materials for a wide range of exploratory studies. Today, thermal scanning probe lithography (t-SPL) has matured into turn-key systems that can be compared to some extend to electron beam lithography, but without the useof charged particles and

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[1] **BID Early Career Researchers Award**

without the need for development. The full grasp of potential applications in R&D and production is still growing as the technique is still emerging.

In this talk, we will give first some background how heated AFM probes were initially designed and fabricated that led to today's advanced thermo-mechanical probe design of micro-cantilevers and nano-tips. The paper will then review some main achievements up to date [3] and then present recent results on t-SPL utilized for 2D materials by our own work [4, 5], and will conclude with some outlook on further challenges in hot-tip nanoengineering.

References:

[1] R. Garcia, et al. Nature Nanotechnology (2014)

[2] H. J. Mamin et al. Applied Physics Letters (1992)

[3] S. T. Howell et al. Microsystems & Nanoengineering (2020)

[4] X. Liu et al. Advanced Materials (2020)

[5] X. Liu et al. Nano letters (2020)

10:40am **MN+AS+NS+QS+SE-MoM-8 Atomically-Thin MoS_2 Nanoelectromechanical Resonators***, R. Yang,* Shanghai Jiao Tong University, China*; **Jaesung Lee,*** University of Texas at El Paso **INVITED**

With the development of the Internet of Things (IoT), new sensors and signal processing elements that consume *near-zero* power to operate on resonance, have high tunability and small form factor are necessary.The ultralow mass and large resonance tunability make resonant 2D nanoelectromechanical systems (NEMS) suitable for ultrasensitive mass, force and biomolecular sensing, radio-frequency (RF) front end, and strain-tunable devices.Further, molybdenum disulfide (MoS_2) resonators only require picowatt level of power for sustaining the strong and stable resonance operations due to their ultralight weight.This opens an opportunity to explore new sensors and signal processing elements for IoT applications that really require near-zero power to operate on resonance, and at the same time, have wide dynamic ranges and tuning ranges. In this talk, we summarize our most recent advances in 2D MoS_2 NEMS resonators.

11:20am **MN+AS+NS+QS+SE-MoM-10 Can a Single Nanomechanical Mode Generate a Frequency Comb?***, **Eva Weig,*** Technical University of Munich, Germany **INVITED**

Doubly-clamped nanostring resonators excel as high Q nanomechanical systems enabling room temperature quality factors of several 100,000 in the 10 MHz eigenfrequency range. Dielectric transduction via electrically induced gradient fields provides an integrated control scheme while retaining the large mechanical quality factor [1]. Dielectrically controlled nanostrings are an ideal testbed to explore a variety of dynamical phenomena ranging from multimode coupling to coherent control [2]. Here I will focus on the nonlinear dynamics of a single, resonantly driven mode. The broken time reversal symmetry gives rise to the squeezing of the string's fluctuations. As a result of the high mechanical Q factor, the squeezing ratio is directly accessible from a spectral measurement [3]. It is encoded in the intensities of the two spectral peaks arising from the slow dynamics of the system in the rotating frame. For stronger driving, an onset of self-sustained oscillation is observed which leads to the generation of a nanomechanical frequency comb. The effect is a consequence of a resonantly induced negative effective friction force induced by the drive. This is the first observation of a frequency comb arising solely from a single mode and a single, resonant drive tone [4].

[1] Q. P. Unterreithmeier et al., Nature 458, 1001 (2009)

[2] T. Faust et al., Nature Physics 9, 485 (2013)

[3] J. Huber et al., Phys. Rev. X 10, 021066 (2020)

[4] J. Ochs et al., in preparation

Manufacturing Science and Technology Group
Room 305 - Session MS+HI-MoM

Machine Learning for Microelectronics Manufacturing Process Control and Materials Discovery R&D

Moderators: Tina Kaarsberg, U.S. Department of Energy, Advanced Manufacturing Office, **Gary Rubloff**, University of Maryland, College Park

8:20am **MS+HI-MoM-1 Advancing Semiconductor Industry Process Control via Data-Centric AI***, **Jeff David,*** PDF Solutions **INVITED**

Data-Centric AI.Over the last several decades, much of the research and work in machine learning has been based on a model-centric approach or software centric approach.[1] In recent years, some of the codebase for core algorithms such as neural networks have reached a level of maturity where those base algorithms now essentially represent a solved problem for a lot of applications.This has created the opportunity to focus more on the data to improve results, where there is still a significant amount of room to improve the approaches to boost overall outcomes.Areas of Data-Centric AI that have received a growing amount of attention recently include[1]: Measuring data quality, Data iteration, Data management tools, and Data augmentation and data synthesis.

While there has been increasing application of Data-Centric AI in other industries, there are also opportunities for the application of Data-Centric AI in the semiconductor industry as well.Below are a two examples of approaches that have been explored and implemented:

Metabinning and generalized model across chip products

It is difficult to train a model using available data that can be applied to other chip products, due to the unique bin assignment across potentially many thousands of products, even though the underlying failure mechanisms at the device level may be similar.A solution to this challenge is to create metabins that group together bin ID's that are the same or very similar, across chip products.By generating metabins as new labels and overriding the original hardbin/softbin ID's (which again may be disparate), a generalized model can be trained with more previously available data and quickly applied to new chip products for failure prediction.

Classification of wafer failure patterns

Key difficulties in applying machine learning to the classification of spatial failure patterns on wafers are the limited number of wafer classifications (labels) and wafer data available to train the model for a new chip product.To address these issues, a Data-Centric AI approach can be applied.The first step is to generate Augmented Data: Wafers with known patterns are generated randomly.Then the new patterns can be quickly added to the model, by expanding the pattern definition library and retraining.Unlike actual data, new patterns from one product type might be considered general learning and useable to upgrade models.

References:

(1)Andrew Ng, NeurIPS Workshop, Data Centric AI, December 2021

9:00am **MS+HI-MoM-3 Paths Toward Autonomous Plasma Process Tool Operation by Pairing of Plasma and Machine Learning Technologies***, **Jun Shinagawa**, P. Ventzek,* Tokyo Electron America Inc., **INVITED**

"Smart manufacturing" initiative is a means to meet automation and process control requirements set by semiconductor device technology that is now far below the 10 nm critical dimension in manufacturing[1]. We present our holistic approach on pairing first principle in-situ plasma diagnostics with machine learning techniques to build key components of autonomous plasma process tool operation system or advanced equipment control (AEC) system. AEC is a multi-module system consisting of plasma monitor and control and fault detection and classification(FDC) modules. Machine learning techniques are used to enhance accuracy and reliability of embedded models in the aforementioned modules.

REFERENCE

[1] SEMI, "What is smart manufacturing?" [Online], Available: https://www.semi.org/en/industry-groups/smart-manufacturing/what-is-smart-manufacturing [Accessed Nov. 30, 2021]

9:40am **MS+HI-MoM-5 Compliant Hybrid Bonding for Large CTE Mismatched Electronic Materials***, **Mieko Hirabayashi Hirabayashi**, M. Wiwi, S. Herrera, E. Madison, M. Jordan,* Sandia National Laboratories

We will discuss methods for hybrid bonding utilizing low modulus materials to enable heterogeneous integration with high density (< 20 µm pitch) interconnections of CTE (coefficient of thermal expansion) mismatched materials. Hybrid bonding techniques, where mechanical stability is provided from a direct bond and electrical connection through a metal-to-metal bond are used to make high-density electrical connections for materials like hybridized CMOS imagers. The temperature of formation of the direct bond and the stiffness of the bonding material result in highly stressed interfaced, limiting the materials that can be used for a hybrid bond.

We demonstrate the joining dissimilar materials utilizing a compliant bonding layer. By changing materials, we allow stress moderation in the bonding layer which reduces the stress on the top and bottom chips. Reliability decreases significantly when the differences in coefficients of thermal expansion (CTE) are large. With large CTE mismatch between a top chip and a bottom chip, one chip expands more than the bottom chip during thermal cycling. If the interface is brittle, the stress due to the difference in CTE induces cracking at the interface. The current method for addressing this issue is to limit the total area bonded –but this limits the advancement of the technology.

This has ramifications for infrared imagers and other applications that combine compound semiconductors with silicon microchips. The size of hybridized infrared imagers, for example, is limited by the mismatch between the different materials that go into them. This presentation will include the methods we have developed to integrate polymers between dissimilar materials to reduce stress due to CTE mismatch and thus increase reliability.

SNL is managed and operated by NTESS under DOE NNSA contract DE-NA0003525

10:40am **MS+HI-MoM-8 Machine Learning Accelerated Scale-up for Microporous Materials - An Industrial Perspective***, **Di Du**, P. Kamakoti,* ExxonMobil Technology and Engineering Company **INVITED**

Microporous materials such as zeolites and MOFs play a crucial role in producing energy and energy products at scale. Traditional approaches for materials development and scale-up are time consuming and involve experience-based trial and error. Two key areas for materials understanding are the critical variables that impact the synthesis and optimization of material properties which are usually described by quantitative synthesis-property relationships (QSPR). This presentation provides an overview of statistical and machine learning approaches to build QSPR. These methods provide a highly efficient path to optimize synthesis parameters towards targets such as purity, crystal size and surface area, and enable us to significantly speed up our materials workflow.

Our workflow combines design of experiments, machine learning, and high-throughput experimentation (HTE). In order to build QSPR, we featurized the characterization data using machine learning and deep learning approaches. For example, we quantified crystal purity using peak deconvolution of powder XRD pattern. We used a deep learning model to calculate crystal size and aspect ratio from scanning electron microscopy (SEM). We performed functional principal component analysis to select the linear region of Brunauer-Emmett-Teller (BET) adsorption curve which is found to be more accurate than Rouquerol's rules. Since the synthesis space for microporous materials is large and complex, we combined Bayesian Optimization and HTE to further accelerate the workflow. The prior knowledge for Bayesian optimization often comes from a sparse matrix. We used an iterative machine learning model to predict and fill the missing values with uncertainty quantification. After optimization, we used feed-forward neural networks to summarize QSPR for extended investigation at different scales.

We validated the accelerated workflow with a known zeolite. Without referring to historical data, we used the workflow to systematically probe a large and complex synthesis parameter space and obtain small pure crystals of the material. The new workflow demonstrated a significant reduction in the number of experiments needed to meet the same goals as past experiments.

11:20am **MS+HI-MoM-10 Optimizing Copper Deposition in High Aspect Ratio Through Silicon Vias***, **Jessica N. McDow**, R. Schmitt, M. Hirabayashi, J. McClain, M. Jordan,* Sandia National Laboratories

We show an optimization method for filling high aspect ratio through silicon vias (TSVs) that provides insights into the diffusion and suppression kinetics of a superfilling electroplating chemistry. In general, TSV copper filling processes are designed to be used with thinned wafers (<200 µm), but some TSV last and microelectromechanical systems (MEMS) require full wafer thicknesses. To electroplate full-wafer thickness TSVs, a suppressor only solution utilizes an s-shaped negative differential resistance (S-NDR) mechanism.[1,2]

This suppression/fill mechanism is sensitive to the via geometry as well as the overpotential during the electroplating. Using a suppressor only chemistry consisting of copper sulfate, sulfuric acid, potassium chloride, and Tetronic 701, we demonstrate a time-dependent process window where early on too high of an overpotential results in suppressor breakdown and too low of an overpotential results in complete suppression of the deposition process. By controlling the voltage between -520 mV (MSE) and -560 mV (MSE), we were able to demonstrate complete fill of the TSVs in 30% of the time previously required for filling. We also hypothesize that there is a maximum void-free fill rate for suppressor only chemistries.

Understanding the filling kinetics provides a throughput target for microelectronic devices. Copper filled TSVs are a key technology for 3D heterogeneous integration. TSV designs improve device functionality, increase bandwidth per volume, simplify assembly, and enable system miniaturization. In this work, understanding of copper deposition kinetics in a suppressor only electrolyte and the development of optimized plating parameters utilizing the S-NDR mechanism is outlined.

SNL is managed and operated by NTESS under DOE NNSA contract DE-NA0003525. SAND2022-7316A

[1] Rebecca P. Schmitt et al 2020 J. Electrochem. Soc. 167 162517.

[2] D. Josell and T. P. Moffat 2018 J. Electrochem. Soc. 165 D23.

11:40am **MS+HI-MoM-11 Advanced Manufacturing using Virtual Metrology and Equipment Intelligence®** *, **David Fried**,* Lam Research Corporation **INVITED**

The semiconductor industry is now confronting a number of metrology and manufacturing challenges due to critical technology requirements at next-node architectures.Advanced patterning techniques, such as EUV, frequency multiplication and selective deposition, are needed to meet cost and variability challenges at smaller line dimensions.Memory technologies, such as NAND, DRAM, and others, are requiring new materials and the transition to 3D topologies that are more challenging to manufacture.Advanced logic (such as GAA architectures) and heterogenous integration are being pursued in order to reduce power, footprint, and speed in next generation devices, but also require new, higher density and more complex manufacturing techniques.These technology requirements are creating additional metrology challenges, such as a need to measure smaller dimensions in complex 3D structures, increased measurement frequencies and additional demands for metrology data integration and analysis.

In this talk, we will discuss innovative concepts to address some of these next node metrology challenges.We will review the concepts of virtual fabrication and virtual metrology, and how they can be used in conjunction with conventional metrology to better support defect analysis and yield optimization at the latest technology nodes.We will also discuss how physical metrology can be used to calibrate a virtual process model, along with how a virtual process model can be used to validate physical metrology measurements made on a 3D NAND device.

In addition, our presentation will review the concept of Equipment Intelligence®, and how sensor-based metrology is being used to improve chamber and fleet variability.We will discuss how data from in-situ and standalone metrology, using machine learning/artificial intelligence, calibrated models, and advanced analytics, can drive real-time feed-forward and feedback optimization. We will show a specific example of next-generation metrology-based optimization, by presenting an advanced, in-situ etch-depth metrology system that uses spectral analysis and machine learning to deliver significant improvements in wafer-to-wafer etch depth control.

In our conclusion, we will summarize the challenges of next node architectures, and discuss how the concepts discussed in this presentation can be used by all participants in the semiconductor technology space to measure, characterize and address these upcoming challenges.

Nanoscale Science and Technology Division
Room 304 - Session NS1+QS-MoM

Fabrication, Testing and Metrology of Quantum Devices and Systems

Moderator: Wonhee Ko, Oak Ridge Natinal Laboratory

8:20am **NS1+QS-MoM-1 Single Electrons on Solid Neon: A New Solid-State Qubit Platform with Ultralong Coherence***, **Xianjing Zhou**,* Pritzker School of Molecular Engineering, University of Chicago **INVITED**

Progress towards the realization of quantum computers requires persistent advances in their constituent building blocks—qubits. Novel qubit platforms that simultaneously embody long coherence, fast operation and large scalability offer compelling advantages in the construction of quantum computers and many other quantum information systems. Electrons, ubiquitous elementary particles of non-zero charge, spin and mass, have commonly been perceived as paradigmatic local quantum information carriers. Despite superior controllability and configurability, their practical performance as qubits through either motional or spin states depends critically on their material environment. In this talk, I will present our experimental realization of a new qubit platform based on isolated single electrons trapped on an ultraclean solid neon surface in vacuum. By integrating an electron trap in a circuit quantum electrodynamics architecture, we achieve strong coupling between the motional states of a single electron and a single microwave photon in an on-chip superconducting resonator [1]. Qubit gate operations and dispersive readout are successfully implemented. Our latest measurements show that both the relaxation time T_1 and coherence time T_2 have reached 0.100-millisecond scale [2]. The observed single-shot readout fidelity, without using a quantum-limited amplifier, is already 94.4%. Simultaneous strong coupling of two qubits with the microwave resonator is also demonstrated, as a first step toward two-qubit entangling gates for universal quantum computing. These results manifest that the electron-on-solid-neon (eNe) charge qubits have outperformed all the existing charge qubits to date and rivaled the state-of-the-art superconducting transmon qubits.

[1] X. Zhou … and D. Jin, “Single electrons on solid neon as a solid-state qubit platform”, Nature 605, 46–50 (2022).

[2] X. Zhou … and D. Jin, “Electron charge qubits on solid neon with 0.1 millisecond coherence time”, manuscript submitted (2022).

9:00am **NS1+QS-MoM-3 Ultra-thin TaN Damascene Nanowire Structures on 300 mm Si Wafers for Quantum Applications***, **Ekta Bhatia**, S. Kar, S. Olson, T. Vo, S. Schujman, J. Nalaskowski,* NY CREATES*; H. Frost,* SUNY Polytechnic Institute, Albany*; J. Mucci, B. Martinick, I. Wells, T. Murray, C. Johnson, V. Kaushik, S. Papa Rao,* NY CREATES

Tantalum nitride (TaN) is a material which has been used as a copper diffusion barrier in integrated circuits, along with many other applications ranging from corrosion-resistant coatings to superconducting quantum devices. Superconducting nanowire single photon detectors (SNSPDs) are critical for applications in photonic quantum computing, single-flux quantum logic circuits for qubit readout, and neuromorphic computing. TaN SNSPDs have been shown to extend the detection bandwidth to longer wavelengths, along with higher detection efficiency, enabling new applications in cosmology when fabricated into large scale arrays. TaN devices at 300 mm wafer scale can leverage the advances made by the semiconductor industry in process control, improving yield, pattern fidelity and wafer-to-wafer predictability of performance. Hence, the development of this process technology will enable large scale SNSPD arrays, and will also be useful for superconducting circuits for quantum applications.

Detailed studies of the influence of nitrogen content on the superconducting characteristics of TaN thin films are not widely available in the literature, particularly at 300 mm wafer scale. We report the development of ultra-thin reactive sputtered TaN films prepared with different Ta to N ratios on 300 mm scale. We fabricated damascene structures of TaN nanowires with widths varying from 100 to 3000 nm and thickness varying from 5 to 35 nm using 193 nm optical lithography and advanced chemical mechanical planarization.

We confirmed a sigmoidal dependence of TaN sheet resistance on Ta to N ratio, and a decrease in crystallite size (extracted from XRD measurements). The superconductor to insulator transition as a function of Ta to N ratio is reported. We will also discuss the influence of encapsulation of the superconducting wires with metallic TaN and copper. Cu encapsulation can improve contact resistance during measurement, and has implications for thermal conduction along the length of the superconducting nanowire. In contrast, adding an intervening layer of highly disordered metallic TaN between the superconducting TaN and Cu ensures minimal leakage of Cooper-pairs at TaN/Cu interface. We will report the variation of T_c and J_c of TaN nanowires as a function of film thickness, material characteristics, Ta to N ratio and encapsulation.The potential of ultra-thin TaN films at 300 mm scale will be discussed in the context of applications such as on-chip integration for readout of superconducting qubits, in quantum phase slip studies, and large focal-plane detector arrays for cosmology.

9:20am **NS1+QS-MoM-4 Direct Integration of Atomic Precision Devices into a MOS-Compatible Process***, **Jeffrey Ivie**, D. Campbell, A. Leenheer, C. Halsey, E. Anderson, S. Schmucker, D. Scrymgeour, X. Gao, W. Lepkowski, T. Lu, L. Tracy, S. Misra,* Sandia National Laboratories

Atomic precision advanced manufacturing (APAM) of electrical devices, fabricated using hydrogen depassivation lithography in a scanning tunneling microscope, offers a way to explore device physics with the ultimate degree of control. Almost all previous work has focused on exploring applications in quantum physics, particularly with a focus on qubits, using devices operating at cryogenic temperatures. While APAM may benefit applications in microelectronics, such as the strong doping of contacts in scaled transistors, the high temperature surface preparation of APAM generally makes it incompatible with modern metal-oxide semiconductor (MOS) process flows. To leverage significant past investments in CMOS manufacturing and enable a wider application space for APAM devices, demonstration of direct integration of APAM into existing MOS process flows is required.

To enable direct integration of APAM devices, we have established a natural insertion point for APAM processing between Front-end-of-line (FEOL) and Back-end-of-line (BEOL) steps on Sandia’s 0.35-micron CMOS node. The insertion point allows for readily accessed device Si through gentle sputtering and thermal annealing, which has a sufficiently crystalline surface critical for APAM delta doping. Integration of the moderate temperature APAM processing step (<600 °C) between high temperature FEOL processing (1000 °C) and before low temperature BEOL processing (<400 °C) maintains the electrical characteristics of both the inserted APAM delta-doped material and the discrete transistors and integrated circuit components from FEOL. Furthermore, accelerated lifetime measurements of APAM wires demonstrate that patterned APAM material is more robust than standard metal features in modern CMOS devices. Establishing the capability of direct integration of APAM into a CMOS process flow opens the door to enhance CMOS transistors with APAM-based processing along with providing wider manufacturing interest. Similarly, implementation of novel APAM-based devices alongside CMOS circuits is a significant discovery platform for microelectronics, neuromorphic computing hardware, or hybrid quantum applications.

This work was supported by the Laboratory Directed Research and Development Program at Sandia National Laboratories and was performed, in part, at the Center for Integrated Nanotechnologies, a U.S. DOE, Office of Basic Energy Sciences user facility. SNL is managed and operated by NTESS under DOE NNSA contract DE-NA0003525. The views expressed in the article do not necessarily represent the views of the DOE or the U.S. Government.

9:40am **NS1+QS-MoM-5 Low Thermal Budget PMOS in Low Temperature Epitaxial Silicon***, **Christopher Allemang**, D. Campbell, J. Ivie, T. Lu, S. Misra,* Sandia National Laboratories

Atomic precision advanced manufacturing (APAM) enables deposition of dopants in silicon (Si) with atomic precision and has been exploited to make donor-based qubits. However, understanding the electrical effects of the process tradeoffs in burying the dopants under an epitaxial Si capping layer grown at low temperatures has remained a challenge, both for qubits and for other microelectronics applications. This cap layer can be deposited at the lowest temperatures to limit the diffusion of dopants, or at modest temperatures to limit the density of point defects. Here, to evaluate the electrical quality of the Si cap, we explore using APAM materials and compatible processes for other microelectronic devices, namely p-type metal-oxide-semiconductor (PMOS) field-effect transistors.

The Si cap is unintentionally doped with aluminum during the growth process leading to a p-type material. To employ this p-type material for PMOS, we must have ohmic contacts and a way to gate the channel. Typical processes used for contacting and gating the channel, e.g. implants and thermal oxide, cannot be used here because they are high temperature processes. To maintain an APAM compatible thermal budget, we have developed ohmic contacts to the cap layer using platinum silicide formed at 400ºC and an atomic layer deposition Al_2O_3 gate oxide grown at 250ºC. These temperatures are also within the back-end-of-line thermal budget for Si CMOS, implying this process could be used to integrate an additional device layer on an existing chip.

The silicide contacts are qualified by fabricating Schottky diodes on n-type material and analyzing their current-voltage (*IV*) characteristics, while the gate oxide is qualified by measuring the capacitance-voltage characteristics of MOS capacitors. Further, these processes are combined to demonstrate PMOS transistor behavior in APAM material for the first time. The electrical transport in the cap layer is then qualified using *IV* measurements. While these results represent the initial qualification of electrical transport in the cap layer, further studies and analysis may reveal impacts to APAM quantum devices.

This work was partially funded by the Advanced Manufacturing Office project Big Energy Efficient Transistors, supported by the Laboratory Directed Research and Development Program at Sandia National Laboratories, and performed, in part, at the Center for Integrated Nanotechnologies, a U.S. DOE, Office of Basic Energy Sciences user facility. SNL is managed and operated by NTESS under DOE NNSA contract DE-NA0003525. The views expressed here do not necessarily represent the views of the DOE or the U.S. Government.

Nanoscale Science and Technology Division
Room 304 - Session NS2+AS+EM+SS-MoM

Quantum Based Sensors and Metrology

Moderator: Nikolai Klimov, National Institute of Standards and Technology

10:40am **NS2+AS+EM+SS-MoM-8 Interfacing Biomolecules with Coherent Quantum Sensors*, Peter Maurer,*** University of Chicago **INVITED**

Quantum optics has had a profound impact on precision measurements, and recently enabled probing various physical quantities, such as magnetic fields and temperature, with nanoscale spatial resolution. In my talk, I will discuss the development and application of novel quantum metrological techniques that enable the study of biological systems in a new regime. I will start with a general introduction to quantum sensing and its applications to nanoscale nuclear magnetic resonance (NMR) spectroscopy. In this context, I will discuss how we can utilize tools from single-molecule biophysics to interface a coherent quantum sensor with individual intact biomolecules, and how this could eventually pave the way towards a new generation of biophysical and diagnostic devices.

Nanoscale Science and Technology Division
Room 304 - Session NS3+EM+TF-MoM

Nanophotonics, Metasurfaces and Plasmonic Systems Including Inverse Design Methods

Moderators: David Czaplewski, Argonne National Laboratory, **Nikolai Klimov**, National Institute of Standards and Technology

11:20am **NS3+EM+TF-MoM-10 Quantum and Nonlinear Photonics in Silicon Carbide with Inverse Design*, Daniil Lukin,*** *J. Vuckovic,* Stanford University **INVITED**

Integrated photonics technology has achieved the degree of scalability and complexity needed for building up photonic quantum computers based on optically-addressable spin qubits such as color centers. However, at present none of the industry-standard photonics materials host high quality color centers. Silicon Carbide has the potential to become a technologically-mature platform that can close this longstanding gap between classical and quantum photonics devices. I will discuss the recent progress of Silicon Carbide integrated photonics for quantum and nonlinear applications, as well as the applications of inverse-design for novel photonics functionalities.

Plasma Science and Technology Division
Room 315 - Session PS-MoM

Plasmas for the Environment and Sustainability: Plasmas-Liquid Interactions, Water, Air, Soil Treatment

Moderators: David Go, University of Notre Dame, **Jeffrey Shearer**, TEL

9:00am **PS-MoM-3 Nitrogen Fixation by Atmospheric Plasma: Effect of Process Parameters on Product Yield and Selectivity***, N. Maira,* Université libre de Bruxelles, Belgium*; A. Remy,* Université libre de Bruxelles, Belgium/ Ghent University, Belgium*; K. Van't Veer,* Université libre de Bruxelles / Antwerpen University, Belgium*; C. Pattyn, N. Roy,* Université libre de Bruxelles, Belgium*; A. Bogaerts,* University of Antwerp, Belgium*; N. De Geyter,* Ghent University, Belgium*; **Francois Reniers,*** Université libre de Bruxelles, Belgium

Nitrogen fixation using atmospheric plasma is a possible alternative route to the Haber-Bosch process. Among these, microplasmas over water, DBD over water and DBD without water can be used to synthesize ammonium, nitrites and nitrates, depending on the reactants used, and the process parameters. The talk will present a summary of results obtained using the 3 types of plasmas mentioned above. Thanks to original setups, the production of nitrogen oxides and ammonia in the gas phase and in the liquid phase will be tracked. It is shown that simultaneous production of nitrates and ammonium can be obtained from pure nitrogen using a microplasma over water (plasma-induced disproportionation). Conditions for nitrite free solutions are established. The effect of the gas composition and the electrodes polarity on the obtained results is shown. The importance of water vapor as a source of OH and H for reactivity is highlighted. For DBDs without water, the influence of the streamers on the NOx synthesis (from N_2 and O_2) and on the NH_3 synthesis (from N_2 and H_2) is evidenced through heat sensitive experiments on one hand, and through modeling on the other hand. It is shown that, for NOx synthesis the streamers temperature have a significant effect on the oxidation mechanism, preventing the ozone route when too hot. For ammonia synthesis, if the streamers are beneficial for nitrogen splitting, it is shown that they also destroy ammonia, which is preferentially formed outside the streamers.

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C. Pattyn et al., Green Chemistry, submitted

C. Pattyn et al., Physical Chemistry Chemical Physics (2020) 22 (42), 24801-24812

K. Van’t Veer et al. The Journal of Physical Chemistry (2020) C 124 (42), 22871-22883

Acknowledgements : this work is funded by the Belgian Excellence of Science (EoS) "Nitroplasm" project.

9:20am **PS-MoM-4 Fundamental Insights Into Plasma-Liquid Interactions by Combined Experiments and Multiphase Modeling*, Necip Uner,*** Middle East Technical University, Turkey*; S. Keniley,* LAM Research*; E. Perez, D. Curreli, M. Sankaran,* University of Illinois at Urbana-Champaign

Plasmas in contact with liquids are of interest because of the complex interactions and potential for novel physical and chemical processes. In general, the system is composed of the gas-phase, liquid-phase, and the gas-liquid interface. Experimental measurements have been made in the gas phase and liquid phase of a plasma-liquid process, and more recently modeling has also been performed. There remains a need to compare experiments and modeling to validate simulation outputs and develop predictive capabilities.

This talk will focus on two important aspects plasma-liquid processes: predicting the species densities and heat transfer phenomena near the interface. The focus of our study was a direct-current (DC) operated pin-to-plane electrode geometry with the liquid serving as an electrolyte and a counter electrode immersed in the solution. First, our recent studies on developing a one-dimensional, isothermal but unsteady-state model for coupled plasma-liquid interactions will be presented. Using a drift-diffusion-reaction formalism, plasma and aqueous chemistry was solved for in an argon-salt water system. In this system, one of the reactions that occurs is the formation of hydroxyl radicals, which subsequently produce hydrogen peroxide. We studied potential mechanisms for hydrogen peroxide production with the plasma operated as either the cathode or anode. Experiments were performed in support of modeling to characterize the plasma and measure the aqueous hydrogen peroxide, and both modeling and experimental results show that its production is substantially higher during anodic operation. Most importantly, the model can successfully predict the order of magnitude of H_2O_2 generation rate in the bulk liquid during anodic operation.

In the second part of this talk, it will be shown that a major portion of the energy in the pin-to-plane electrode is dissipated as heat during cathodic operation. Optical emission spectroscopy indicates that even for a discharge power of less than 2 W, the gas temperature may surpass 1000 K in the cathode sheath, which subsequently heats up the electrode. For small electrode geometries, cathode heating is visible due to extensive blackbody radiation, which confirms the gas temperatures measured by spectroscopy. Despite being only 1 mm away from the cathode, infrared thermometry indicates that the water interface remains surprisingly cool, reaching a maximum of only 335 K. These findings suggest that in addition to the inherent local non-equilibrium between the electrons and larger species in the plasma, there exists a very strong thermal non-equilibrium across the plasma as well.

9:40am **PS-MoM-5 Merging the Fundamental and Applied: Understanding Plasma Kinetics and Energetics to Build Better Mousetraps***, **Ellen Fisher**[1],* University of New Mexico **INVITED**

Historically, plasmas have been used extensively to increase the functionality of a myriad of materials for use in a wide range of applications.Despite this storied history, use of plasma-processed materials has been limited by a lack of understanding of fundamental mechanisms.Moreover, the applicability of various processes such as plasma-assisted catalysis is also limited by this lack of knowledge on the basic kinetics and energetics that contribute to plasma-catalyst synergy.This presentation will review a range of systems that have benefited from the use of optical spectroscopy to investigate gas-phase processes in inductively-coupled plasma systems revealing physical and chemical properties of the plasma systems.Perhaps more importantly, these data highlight details of molecule excitation pathways occurring in various plasma systems as well as how various species are involved in gas-surface interactions.Combined with materials characterization studies, these results emphasize the intimate connections between substrates, plasma parameters and fundamental plasma properties, all crucial components to creating better mousetraps.

10:40am **PS-MoM-8 Comparative Investigation of DC Plasma Versus Boron-doped Diamond Electrodes for Electrochemical Degradation of PFOA***, **Jasmine Dinari**,* University of Illinois at Urbana-Champaign*; N. Uner,* Middle East Technical University, Turkey*; P. Baldaguez Medina, M. Sankaran, X. Su,* University of Illinois at Urbana-Champaign

Per- and polyfluoroalkyl substances (PFAS) are a group of persistent man-made chemicals, currently found in water, that stagnate in the environment. There is a need to degrade PFAS such as perfluorooctanoic acid (PFOA) in our water supplies. In the last decade, two methods that have attracted attention for their capability of mineralizing PFAS into fluoride and CO2 are electrochemical processes and plasmas formed at the surface of a liquid.

Here, we performed a comparative investigation of a plasma and one of the most well-studied electrochemical electrodes, boron-doped diamond (BDD), for PFOA degradation. In addition to carrying out the experiments in the exact same direct-current (DC)-powered electrochemical setup, the plasma and BDD were operated as either the anode or the cathode, with the same platinum wire mesh as the counter electrode. While both the BDD and plasma achieved almost complete degradation of PFOA, the optimal configuration for each of them was found to be cathodic for the plasma and anodic for the BDD, with the plasma degrading the PFOA almost 3 times faster. Compared to the BDD, the plasma required more than an order of magnitude higher voltage, but lower current to achieve a similar degradation efficiency. As a result, both the plasma and BDD degradation resulted in similar energy efficiencies.

Fundamentally, the BDD electrode exhibited zero-order kinetics, revealing that PFAS degradation using the conventional electrochemical method was kinetically controlled. On the contrary, analysis using a film model indicated that the plasma degradation kinetics was mass-transfer-controlled because of the extremely rapid reaction kinetics. In addition, we found that in the case of the plasma electrode, the counter electrode played a critical role. Combined with their optimal configurations, these results suggest that an asymmetric device with the plasma as the cathode and the BDD as the anode may lead to enhanced degradation.

11:00am **PS-MoM-9 Integrated circuit Manufacturing with Plasma Activated Chemical Treatment (IMPACT): A Potential Approach for Reducing the Dose-to-Clear in a Commercial Photoresist***, **Christian Williams**, S. Dubowsky, E. Barlaz, S. Marcinko, M. Sankaran,* University of Illinois at Urbana-Champaign*; E. Suga, A. Matsuyama,* TOK America, Japan*; D. Curreli, D. Ruzic,* University of Illinois at Urbana-Champaign

One of the main characteristics that determine how suitable a photoresist formulation is for industrial applications is referred to as the “dose-to-clear”, defined as the amount of energy from the light source necessary to remove (in this case positive) resist from the exposed area. This is an important factor when it comes to chemically amplified resists (CARs), as there is a trade-off between line edge roughness and the dose provided. The Illinois Plasma Institute (IPI) along with the Center for Plasma Material Interactions (CPMI) have developed a method[1] where the polymer component of two commercially available photoresists (designed for wavelengths of 193 nm and 13.5 nm) are treated with an atmospheric AC jet plasma with the intent of reducing the bond energies in the polymer. Some Density Functional Theory (DFT) modeling done at the Laboratory for Computational Plasma Physics (LCPP) indicates the injection of a charged species, in this case, solvated electrons can lower the bond energy of polymers such as those commonly used in commercial photoresist formulations. Preliminary experimental results indicate that the treatment leads to the ability of the resist to be removed at lower exposure times (lower dose) for the 13.5 nm resist by up to 20%. There has also been some experimental evidence that there is a reduction in the residue present after the same exposure times between the untreated and plasma-treated samples when using the 193 nm resist. The exposure tool of choice was a 172 nm VUV lamp that is commercially available and was created by Cygnus Photonics. These results were obtained using an optical profilometer to measure the size of the mask patterns and the reductions that take place at varying exposure times. Rheometry (viscosity) measurements have also been done to ensure that the observed effect is not due to reducing the viscosity and therefore the film thickness. Results from a time-dependency study, to determine if the effects are temporary or permanent, will also be discussed in the context of commercial viability and product shelf life, as this will factor into the usefulness of the project in an industrial context. Ongoing efforts towards a pulsed DC plasma jet setup will be discussed as well.

[1] Patent application submitted Nov. 2020

11:20am **PS-MoM-10 Low Power Degradation of Perfluorooctane Sulfonate (PFOS) in Water Using a Nanosecond Pulsed Atmospheric Pressure Plasma***, **Michael Johnson**,* Syntek Technologies*; W. Maza, V. Breslin,* Naval Research Laboratory, Chemistry Division*; D. Boris, T. Petrova, S. Walton,* Naval Research Laboratory

The prevalence and persistence of perfluoroalkyl substances (PFAS) has led to significant concerns over the damage they can have on human health and the environment, particularly when they contaminate bodies of water. Plasma-based water treatments offer a potential solution to this issue, as they offer a rich chemical environment that can degrade contaminants and are flexible enough to operate in different geometries. In particular, atmospheric pressure plasmas driven with short, high voltage pulses produce the requisite chemistry while maintaining high energy efficiency. In this work, a plasma driven with high-voltage (>10 kV) pulses of varying duration (50-400 ns) and frequency (0.5-10 kHz) is investigated for degrading perfluorooctane sulfonate (PFOS) in water. It was found that after exposure to the plasma caused the concentration of PFOS in solution to decrease with repeated passes through the reactor. Increasing the power consumption of the plasma, either by increasing the pulse width or the frequency, improved the rate of PFOS loss but decreased the energy efficiency. For instance, reducing the frequency of the pulse from 10 kHz to 500 Hz decreased the power consumption by over an order of magnitude while requiring about twice as much time to reduce 50% of the PFOS signal. Time-averaged emission spectroscopy showed that increasing the frequency decreased the average electron density of the plasma and while increasing the temperature of the reactor. In contrast, increasing the pulse width from 50 ns to 400 ns did not have a significant impact on the average

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[1] **2020 PSTD Plasma Prize Winner**

electron density or the reactor temperature. Infrared (IR) measurements of the reactor indicated that changes in operating conditions caused only modest changes in reactor temperature. Spectroscopy revealed the presence of photons with energies >5 eV were also observed and could contribute to PFOS loss. This work shows that the main factor determining PFOS loss is the contact time between the plasma reactor and the solution, which implies the most energy efficient operating parameters for PFOS degradation comes from minimizing the duration and frequency of the high-voltage pulses to reduce power consumption.

Surface Science Division
Room 319 - Session SS+AS+TF-MoM
Dynamics and Mechanisms at Surfaces and Interfaces

Moderator: Eric Altman, Yale University

8:20am **SS+AS+TF-MoM-1 Stereodynamics Effects in Grazing-Incidence Fast-Molecule Diffraction***, **Cristina Díaz**,* Universidad Complutense de Madrid, Spain **INVITED**

Grazing-incidence fast-projectile diffraction, measured experimentally for the first time in 2007[1,2], has been proposed both as a complement and an alternative to thermal-energy projectile scattering, which explains the interest that this technique has received in recent years, especially in the case of atomic projectiles (GIFAD)[3,4]. Grazing-incidence fact-molecule diffraction (GIFMD), on the other hand, has received much less attention (mostly theoretical[5,6]), despite the fact that the H_2 molecule:(i) is as easy to generate as atomic H (a widely used projectilein GIFAD experiments); (ii) is lighter than He (another widelyused projectile in GIFAD), which would further reduce surface-phononsinelastic processes; and (iii) can reveal aspects of thesurface landscape that may be relevant in other contexts dueto the internal degrees of freedom (DOFs) and, in the case ofthe ionic surfaces, to the interaction of its quadrupole momentwith the electric field created by the ionic crystal, which is verysensitive to the surface details.Here, we present a theoretical study of grazing-incidence fast-molecule diffraction of H_2 from KCl(001) usinga six-dimensional density functional theory based potential energy surface and a time-dependentwavepacket propagation method. The analysis of the computed diffraction patterns as a function ofthe molecular alignment, and their comparison with the available experimental data, where the initialdistribution of rotational states in the molecule is not known, reveals a puzzling stereo dynamics effectof the diffracted projectiles: Diffracted molecules aligned perpendicular, or quasi perpendicular,to the surface reproduce rather well the experimental diffraction pattern, whereas those moleculealigned parallel to or titled with respect to the surface do not behave as in the experiments. Theseresults call for more detailed investigations of the molecular beam generation process.

1- P. Rousseau, et al., Phys. Rev. Lett., 98, 016104 (2007).

2- A. Schuller et al., Phys. Rev. Lett., 98, 016103 (2007).

3- H. Winter and A. Schuller, Prog. Surf. Sci., 86, 169 (2011).

4- M. Debiossac, P. Pan and P. Roncin, Phys. Chem. Chem. Phys., 23, 7615 (2021).

5- M. del Cueto et al., Phys. Chem. Chem. Phys., 19, 16317 (2017).

6- A. S. Muzas et al., Phys. Rev. B, 96, 205432 (2017).

9:00am **SS+AS+TF-MoM-3 Intermolecular Interactions in Carbonyl Compounds Trigger Surface Reactivity***, **Swetlana Schauermann**, S. Attia, C. Schroeder, M. Schmidt,* Kiel University, Germany

Hydrogenation of carbonyl compounds is an important step in many applications in heterogeneous catalysis. This class of reactions is, however, experimentally highly challenging as it requires the activation of a normally very stable C=O bond. There is an ongoing discussion on an alternative mechanism of C=O bond hydrogenation, which involves keto-enol tautomerization as a first step. In this mechanism, a H atom transfers to oxygen in an intramolecular process to produce a C-O(H) single bond, leaving behind a C=C double bond and forming the enol species. Several theoretical studies predict a significantly lower activation barrier for hydrogenation of the C=C bond in enol as compared to the direct hydrogenation of the C=O bond in ketone for different classes of mono- and dicarbonyl compounds.

In this contribution, we present a mechanistic study on atomistic-level mechanisms of enol formation and stabilization via lateral interactions with co-adsorbed surface species over catalytically active metal surfaces (Pt and Pd).[1, 2] We employ a broad range of carbonyl compounds including acetophenone, acetylpyridine, butanal and ethyl pyruvate, whose adsorption and reactivity behavior were investigated using a combination of infrared reflection absorption spectroscopy (IRAS), scanning tunneling microscopy (STM) and molecular beam techniques. We found that enols can be efficiently formed in different types of carbonyl-containing molecules, however, they require stabilization on the surface via lateral interaction, e.g. by establishing hydrogen bonding between the –OH group of an enol and a carbonyl group of the neighboring adsorbate. Stabilization of formed enols via lateral interactions with the adjustment molecules results in formation of different types of oligomers, including one of more enol molecules. The efficiency of enol formation was found to strongly depend on the chemical structure of the adsorbates and can be affected by e.g. the insertion of the functional groups, such as phenyl or pyridine groups. Also the presence of subsurface hydrogen in Pd was shown to strongly enhance keto-enol tautomerisation in some of the investigated carbonyls. Finally, we provide the first experimental evidence for a low-temperature hydrogenation pathway of carbonyl compounds, which occurs in ketone-enol dimers of acetophenone formed on Pt.[3] In this process, stabilization of enol species via lateral interactions with a neighboring carbonyl is crucial for enabling the target hydrogenation pathway.

2. Attia, S. et al *Angew. Chem. Int. Edit.* **2018,***57*, 16659.
3. Attia, S.et al *ACS Catal.* **2019,***9*, 6882.
4. Attia, S. et al, *J. Phys. Chem. C* **2019,***123* (48), 29271.

9:20am **SS+AS+TF-MoM-4 Velocity Map Images of Subsurface Oxygen Desorbing from Rh(111)***, **Arved Cedric Dorst**, T. Schäfer,* University of Göettingen, Germany*; D. Killelea,* Loyola University Chicago

In heterogeneous catalysis, the reactivity of for example oxidation reactions is often enhanced by transition group metal surfaces as catalysts. After exposure, the oxygen molecules readily dissociate into oxygen atoms on the surface forming characteristic surface reconstruction patterns. However, not only the formation of surface oxygen (O_{surf}) structures but also of subsurface oxygen (O_{sub}) phases is possible, especially when aggressive oxidation agents such as NO_2 or atomic oxygen are used as oxygen source. The O/Rh(111) has been adapted as a benchmark system for O_{sub} formation in the past. In temperature programmed desorption (TPD) experiments, O_{sub} emerges as a narrow desorption feature around 800 K, while O_{surf} forms a subsequent broad desorption feature over several 100 K. Although extensive research has been done on the formed reconstructions of O_{surf}, few is known about the microscopic details of O_{sub} formation.

In the here presented work, velocity map imaging (VMI) was applied to the O/Rh(111) system. We combined TPD and VMI to investigate recombinatively desorbing O_{sub} from Rh(111). This allows a precise assignment of high-resolution velocity distributions of desorption products to certain TPD peaks. We observe a hyperthermal velocity distribution for recombinatively desorbing oxygen from subsurface as well as from surface states. These results provide valuable benchmark data, on which theoretical models describing subsurface oxygen dynamics can be developed and tested.

9:40am **SS+AS+TF-MoM-5 In-Situ Characterization of O_2 Gas-Induced Rearrangement of Near-Surface Composition in Refractory High-Entropy Alloys***, H. Kersell,* Oregon State University*; X. Fan,* University of Tennessee Knoxville*; A. Herman,* Oregon State University*; Z. Lyu,* University of Tennessee Knoxville*; B. Steingrimsson,* Imagars LLC*; P. Liaw,* University of Tennessee Knoxville*; **Gregory S. Herman**,* Oregon State University

Alloy formation enables the enhancement of material properties from electrical and thermal conductivity, to magnetism, chemical reactivity, and mechanical strength and ductility. For example, Ti alloys are lightweight, corrosion resistant, have low Young's modulus, and possess tunable strength and ductility at high temperatures. Their corrosion resistance and low Young's modulus make them suitable for biomedical implants, while their light weight, tunable strength, and high working temperatures facilitate use in high-temperature applications. Traditional alloys often contain a principal metal comprising most of the alloy composition, with additional functionality (e.g., oxidation resistance) induced by minority components. In contrast, high-entropy alloys possess multiple principal components, and have recently attracted significant attention for their enhanced tunability and sometimes unexpected physical properties.

Using ambient pressure X-ray photoelectron spectroscopy (AP-XPS), we have probed the initial oxidation of $TiZrHfNb_{0.3}$ refractory high-entropy alloys (RHEAs). Sputter-cleaning the as-cast alloy in ultrahigh vacuum removes adventitious carbon and native oxides, revealing a metallic alloy containing metal carbide species through its bulk. Subsequent vacuum annealing from room temperature (RT) to 100° C enriches the near-surface carbide content. This near-surface carbide enrichment continues with increasing temperature, accompanied by the formation of surface hydrocarbon species. Meanwhile, the relative compositions of Ti, Zr, Hf, and Nb are stable across the same temperature regime in vacuum. Despite their thermal stability, freshly sputter-cleaned, metallic alloy surfaces exposed to 1 mTorr of O_2 gas become enriched by a near-surface layer of Hf- and Zr- oxides. At the same time, the carbide component is suppressed, and a metal-oxide interface, containing Ti- and Zr- oxides, appears within the XPS probing depth (~8 nm). Subsequent RT oxygen exposure at higher O_2gas pressures induces comparatively minor changes in the surface oxide layer composition.

These results reveal the formation and nature of a thin protective oxide layer at the $TiZrHfNb_{0.3}$ RHEA surface in response to mild oxygen pressures. We present these results in terms of the O_2 pressure/temperature parameter space and discuss implications for the $TiZrHfNb_{0.3}$ RHEA behavior.

10:00am **SS+AS+TF-MoM-6 Surface Faceting and Oxidation in Binary and Ternary Ni-Based Alloys***, **Devin Jessup**, K. Orson, Z. Harris, P. Reinke,* University of Virginia

Future-proofing materials against degradation and failure means designing alloy systems with corrosion resistance built-in, and this is especially important for alloys in extreme environments. Ni-based superalloys are alloyed with Cr, Mo, and W which help form protective layers that are highly corrosion resistant mostly due to chromia (Cr2O3) formation. On polycrystalline alloy surfaces a wide range of crystallographic orientations coexist and are defined by the individual grains. For these often highly stepped or kinked surfaces, a complex surface faceting results from the tendency to minimize the surface free energy leading to an alloy with variable and complex surface topographies. Prior research indicates that different oxide species will nucleate along specific orientations resulting in oxide layer heterogeneity, which can introduce points of failure in the protective layer. Our work focuses on how these differences in surface crystallographic orientation can result in changes in the nucleation and growth of NiO and chromia, whose growth is kinetically controlled under our oxidation conditions.

A Ni11wt%Cr6wt%Mo alloy sample with large grains up to 1 mm offering a wide array of crystallographic orientations was selected for characterization. Scanning Tunnelling Microscopy (STM), Electron Backscatter Diffraction (EBSD), and Scanning Electron Microscopy (SEM) are used to characterize the surface. The native oxide was removed by annealing to 640˚C, and the highly variable surface topography was studied over a range of grains catalogued by EBSD. The alloy shows several unique surface topographies which are controlled by crystallographic orientation. Several examples are included in the supplemental material, which include wave-like facet structures, sharply terminating saw-tooth facets, and flatter “matchstick” structures. These can be correlated with the Miller index of the underlying grain surface on the stereographic triangle. The surface morphology was quantified with respect to facet size, shape, heights, orientation, and spatial distribution. This analysis provided the Miller indices for all well-expressed facets. Grain orientations were matched with their surface structures through a combination of feature matching between SEM and STM imagery and Fast Fourier Transform analysis. Further work will observe oxide nucleation on these facets, and their impact on oxide formation and performance. Understanding these mechanisms will contribute to our understanding of how to design Ni-based alloys for the most stable protective layer.

10:40am **SS+AS+TF-MoM-8 Medard W. Welch Award Talk: Atomistic Simulations to Advance Surface Science***, **Susan Sinnott**[1],* Pennsylvania State University **INVITED**

Computational methods are useful tools in the investigation of atomic and molecular dynamics and associated mechanisms at surfaces and interfaces. Physics-based classical potentials are a class of computational method that is useful for use in classical atomistic simulations of systems made up of thousands to many billions of atoms. These potentials consist of parameterized functions that capture aspects of atomic and molecular interactions within these material systems.

The focus of this presentation is on the third-generation charge-optimized many body (COMB3) potential. COMB3 was developed to enable an atomic-scale description of systems that include combinations of metallic, ionic, and covalent bonding under the same framework. The framework enables the system to determine the charge state of an atom or ion and manifest the physically appropriate type(s) and strength of local bonding as a function of environment correctly and autonomously. The framework further includes a combination of atomic-specific, bond-specific, bond-angle-specific parameters; the former is the same regardless of material, and only new bond-specific and bond-angle-specific parameters are required to extend existing elements to new compounds.

This presentation will provide an overview of the COMB3 potential and illustrate its utility in the study of water-metal surface and nanoparticle interactions, the examination of carbon nanoparticle-metal surface interactions, and the mechanisms associated with the growth of metal films on metallic and oxide substrates.

11:20am **SS+AS+TF-MoM-10 STM Study of Ag Encapsulation of Pd and Pt Islands on Ag(111) at Room Temperature***, **Buddhika Alupothe Gedara**[2], M. Trenary,* University of Illinois - Chicago

PdAg and PtAg bimetallic catalysts are used in many important industrial applications. Therefore, an atomic scale understanding of these catalysts is important for their further development. In this study, the initial stages of submonolayer growth of Pd and Pt islands on Ag(111) at room temperature were investigated using scanning tunneling microscopy (STM). Although Pd (1.7 J m^{-2}) and Pt (2.2 J m^{-2}) have higher surface free energies than Ag (1.1 J m^{-2}) and a similar lattice mismatch (PdAg = 4.8% and PtAg = 4.2%), Pd and Pt show different behavior after deposition on Ag(111) at room temperature. Hexagonal Pd islands are formed on Ag(111) regardless of the coverage. In contrast, Pt shows a high density of small clusters and larger islands indicating less mobility for Pt than Pd on Ag(111). Due to Pd atom place exchange with Ag atoms, Pd-rich brims were observed at the ascending Ag step edges. But, Pt-rich brims were not observed. Because of the absence of Pt-rich brims , removal of Ag atoms created bays at the step edges. Surface Ag atoms migrate to cover both Pd and Pt islands, even at room temperature, creating vacancy pits on the Ag(111) surface. In addition to large vacancy pits, small mobile vacancy pits were observed on Pt/Ag(111). Pd and Pt islands show different moire structures on Ag(111) even though they have almost same lattice mismatch. Migrated Ag atoms nucleate near the center of Pd islands to grow the second layer, whereas, migrated Ag atoms nucleate at the corner of the Pt islands.

Thin Films Division
Room 316 - Session TF+EM-MoM
Microelectronics and Spintronics Application
Moderator: John F. Conley, Jr., Oregon State University

8:20am **TF+EM-MoM-1 Rare Earth Thin Oxide Films for Sustainable Energy***, **Ivona Z. Mitrovic**, H. Finch, S. Almalki, S. Tekin, L. Jones, V. Dhanak,* University of Liverpool, UK*; A. Hannah, R. Valizadeh,* STFC Daresbury Laboratory, UK*; A. Renz, V. Shah, P. Gammon, P. Mawby,* University of Warwick, UK **INVITED**

An ever-greater impetus towards global net zero by 2050 has been driving research in sustainable electronics. This talk will give overview of research led at Liverpool on oxide thin films to be considered as high dielectric constant (high-k) dielectrics on (i) wide band gap (WBG) semiconductor materials for power electronics applications; and in (ii) metal-insulator-metal (MIM) configurations as rectifiers in infrared frequency rectennas for energy harvesting. The WBG semiconductor materials such as GaN and 4H-SiC have emerged as contenders to replace Si in many power electronics applications. High-k oxide materials are necessary for improved electrostatic control over the channel and improved on-current, which in-turn results in higher transconductance for GaN based Metal-Insulator-Semiconductor High Electron Mobility Transistors (MIS-HEMTs). Furthermore, the use of SiO_2 proves to be a bottleneck in exploiting full potential of SiC technology largely due to the unavailability of a reliable high-k dielectric alternative. In this paper, the two rare earth oxide films, Y_2O_3 and Sc_2O_3, prepared by sputtering, have been investigated in terms of

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[1] **Medard W. Welch Award Winner**

[2] **SSD Morton S. Traum Award Finalist**

their band alignment and interface properties on both GaN and 4H-SiC substrates using variable angle spectroscopic ellipsometry and X-ray photoelectron spectroscopy. Furthermore, this study includes applicability of Sc_2O_3 for use in MIM diodes for rectenna. The comparison to state of the art devices that mainly include Al_2O_3 and HfO_2 films has been discussed with the aim of paving the way forward for rare earth thin oxide film applications in driving sustainable future.

Acknowledgement. The UKIERI IND/CONT/G/17-18/18 and F.No.184-1/2018(IC) project funded by the British Council; UKRI GCRF GIAA award 2018/19, EP/P510981/1 and EP/K018930/1, funded by the EPSRC, UK.

9:00am **TF+EM-MoM-3 TaN Electrical Barrier for High-k MOS Capacitor**, *R. César, **José Diniz**,* University of Campinas - UNICAMP, Brazil*; R. Cotrin, E. Joanni, M. Vidal,* Renato Archer Information Technology Center, Brazil

Tantalum nitride (TaN) thin films were used at the interface between high-k titanium oxide (TiO_2) and the silicon substrate. The TaN films were deposited by RF sputtering and three thicknesses 2, 4 and 6 nm were studied. The structural characterization of the films was performed AFM, SEM and EDS. Using the AFM and SEM technique, it was possible to note that the film is formed by different grain sizes (Annex Fg.1). Using the EDS technique, it was possible to map the chemical elements that make up the TaN film, and it was possible to determine that 93,4% of the TaN film is composed of tantalum and 6,6% is composed of nitrogen.

MOS capacitors were developed using n-type silicon and TiO_2 as the gate dielectric. This oxide was deposited by ALD and has a thickness of 35 nm. Between the oxide and the silicon, TaN was deposited by RF sputering and has a thickness of 2, 4 and 6 nm. These devices have the upper electrode in the square shape and varying its dimension. Tables 1 and 2 in the Annex present the parameters calculated and extracted from the CxV and IxV curves of the MOS capacitors with TaN/TiO_2.

The capacitor with 6 nm of TaN did not present well-defined electrical measurements. This may be due to its thickness which started to act as a resistor between the TiO_2/Si. It can be seen from Tables 1 and 2 (Annex) that, 4 nm of TaN showed higher V_{FB} values than the capacitors with 2 nm of TaN. As seen in the structural characterization of the TaN films, the film has 93.4% tantalum. This metal ion is acting as a potential barrier on the capacitor. The higher the barrier, the higher the voltage must be for the device to work.

The capacitor with 2 nm of TaN showed higher hysteresis values than the 4 nm film, as shown in Tables 1 and 2. The 2 nm and 4 nm TaN capacitors showed $C_{máx}$ in the order of $e^{-4} \sim e^{-5}$ F and $e^{-4} \sim e^{-6}$ F, respectively. The same behavior can be described for $C_{mín}$ values. Both capacitors showed minimum capacitance on the order of $e^{-5} \sim e^{-6}$ F.

Both capacitors presented effective charge density (Qo/q) in the order of $e^{17} \sim e^{20}$ /cm^2. This result confirms that tantalum metal ions from the TaN film are interacting with the silicon substrate. Confirming the changes in the values of V_{FB}, $C_{máx}$ and $C_{mín}$. This indicates that variations in the dipole are occurring at the $TiO_2/TaN/Si$ interface, due to chemical reactions between the two materials. These variations in the dipoles can change the value of the flat band voltage making it positive, which is the case for the two TaN film capacitors.

9:20am **TF+EM-MoM-4 Internal Photoemission (IPE) Spectroscopy Measurement of Interfacial Barrier Heights in Pristine and Poled Ferroelectric Hafnium Zirconium Oxide Devices**, ***Jessica Peterson**,* Oregon State University*; T. Mimura,* Gakushuin University, Japan*; J. Ihlefeld,* University of Virginia*; J. Conley,* Oregon State University

Ferroelectric $Hf_{0.5}Zr_{0.5}O_2$ (HZO) has attracted interest for CMOS memory and logic due to ease of integration as HfO_2 is already widely used. After device preparation, a "waking" process involving repeatedly sweeping a field across the material is necessary to induce ferroelectric behavior.[1] Use of HZO in CMOS applications requires knowledge of interfacial energy barriers in the specific film stacks used. Internal photoemission (IPE) spectroscopy is the only method of measuring barrier heights in working devices. IPE measurements of energy barriers have been reported for as-deposited HZO.[2] Here we investigate how waking and poling impact barriers.

20 nm thick HZO was deposited on a TaN coated Si substrates via atomic layer deposition (ALD) using 102 supercycles of HfO_2 (TDMAH) and ZrO_2 (TDMAZ), then coated with a 20 nm blanket TaN film and annealed at 600°C for 30 seconds. The top TaN layer was then stripped before depositing an optically transparent top electrode of 5 nm TaN / 5 nm Pd. Devices were woken by performing 5000 ±5V cycles. Woken devices were poled by applying a 0 to +4V or 0 to -4V square pulses. IPE measurements were taken by applying a voltage to the bottom electrode while grounding the top electrode. Positive (negative) polarity was used to assess the top (bottom) barrier. At each applied field, $\mathcal{E}_{app}$, photon energy incident on the top electrode was swept from 2 to 5 eV. Extracted spectral thresholds were plotted vs. $\mathcal{E}^{1/2}$ and extrapolated to zero field to account for any Schottky field induced barrier lowering.

For unwoken devices, the top and bottom HZO/TaN barriers were 2.6 and 2.9 eV, respectively, indicating the influence of processing. The waking process caused an increase in the top barrier to 2.9 eV while the bottom barrier was unchanged within error. Positive poling caused a reduction in both top and bottom barrier heights to 1.9 and 2.5 eV, respectively, for positive sweep first. Negative poling caused a reduction in top and bottom barrier heights to 2.1 and 2.2 eV, respectively, for negative sweep first. While field sweep direction did not impact barrier heights on pristine devices, it did have a small impact on poled devices, to be discussed. The lower barrier heights for poled devices and polarity dependence are consistent with a recent report on the impact of cycling on TiN effective work function on HZO, and suggest a role for oxygen vacancy migration.[3] This work provides insight into the impact of waking and poling on barriers in HZO devices, information needed for integration.

[1] Grimley et al., AEM 2, 1600173, (2016).

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11:00am **TF+EM-MoM-9 On-Chip ALD LiPON Capacitors for High Frequency Application**, *K. Ahuja,* University of Maryland, College Park*; V. Sallaz, F. Voiron,* Murata, France*; P. McCluskey, G. W. Rubloff,* University of Maryland, College Park*; **Keith E. Gregorczyk**,* University of Maryland

The increase in demand for miniaturized portable electronics has led to increased use of capacitors for power conditioning applications. In order to increase the efficiency of the electronic circuits, the ICs embedded in these devices require stable DC supply voltage, this requires optimization of power distribution networks (PDN). A common approach consists of placing a decoupling capacitor close to the ICs thus shorting the inductive path that limits the current flowing from the slow and distant battery and thus increasing the efficiency of the system. The traditional aluminum electrolytic capacitors and MLCCs are used for this application but they are limited by high intrinsic parasitic inductance, bulky volume, rigid shapes, and low energy density. Next-generation devices with solid-state electrolyte (SSE) using atomic layer deposition (ALD) provide a few advantages to such applications. (1) Thin, ionically conductive materials allow for significant device dimensions reduction avoiding the above-mentioned problems, (2) easy integration with semiconductor chip manufacturing, and (3) an active community developing new materials regularly.

Here, we demonstrate ALD of ultra-thin film lithium phosphorus oxynitride (LiPON) as an inorganic SSE exhibiting both EDLC and electrostatic behavior. Two polymorphs of ALD LiPON ($Li_{3.47}PO_{3.43}N_{0.24}$ and Li_2PO_2N) are deposited between gold current collectors on silicon wafers. The ionic conductivity of the polymorphs is 6.82× 10^{-8} S/cm and 5.42× 10^{-7} S/cm respectively. The ionic conductivity was determined to be the most important metric effecting the charge storage mechanism. Both the LiPON capacitors exhibit an electric double layer behavior with a capacitance of 15 uF/cm^2 and a low leakage current (<20 nA/cm^2) at 2V. The $Li_{3.47}PO_{3.43}N_{0.24}$ shows EDLC behavior up to 1 kHz at 55°C whereas the Li_2PO_2N shows a similar behavior up to 10 kHz. Beyond this frequency, both the polymorphs show an electrostatic behavior with a high dielectric constant (13).

These results highlight the advantage of ALD LiPON as thin-film SSE for capacitors that shows EDLC behavior to an extended frequency limit (10kHz) for state-of-the-art applications. The electrostatic behavior observed at high frequency (>10 kHz) further expands the application window for high-frequency decoupling applications. The high energy density and on-chip integration allow for easier process control and design flexibility for advanced PDN. Further, utilization of ALD's inherent conformality in 3D nanostructures can extend the reach of these solid-state ionic capacitors to increasing energy density metrics along with on-chip integration.

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11:20am **TF+EM-MoM-10 Designer Heusler Half-Metals for Ultra-Fast Spintronics*, Avik Ghosh,*** University of Virginia **INVITED**

Heusler alloys have several interesting attributes, such as a practical realization of the Slater-Pauling rule for half-metallicity with nearest neighbor interactions. Using Density Functional Theory we scavenged through a large number (1359) of full, half and inverse Heuslers, verified their thermal (heat of formation) and chemical (complex Hull distance) stability, and identified multiple potential Slater-Pauling semiconductors and half-metals (e.g. Fe2MnGe, layered Fe1.5TiSb, Co1.5TiSn). In addition, we found some zero momentum half-metals with negative formation energy, materials that are potentially insensitive to magnetic fields while carrying substantive spin currents. Interestingly, uniaxial anisotropy is seen to be induced in some of the L21 and C1b Heuslers (e.g. NiMnSb, CoTiSn) adjoining MgO without losing their half-metallicity, yielding potential magnetic electrode materials with large ballistic tunnel magnetoresistances. Finally, spin flip scattering rates are calculated with KKR and ballistic currents using quantum kinetics, showing that some of these Heuslers have low spin damping, making them good potential candidates for supporting room temperature, ultra-small Neel skyrmions.

Vacuum Technology Division
Room 301 - Session VT-MoM

Vacuum Measurement and Gas Analysis and Vacuum Technology for Quantum Applications

Moderator: James Fedchak, National Institute of Standards and Technology

8:20am **VT-MoM-1 "Much to Do About Nothing:" Advancing Compact UHV Packages for a "Quantum Everywhere" Future*, Alex Tingle,*** ColdQuanta **INVITED**

The burgeoning quantum industry demands scientific and engineering innovation at a breakneck rate. Beyond invention and supply chain challenges of current and near-term laboratory-scale quantum systems, the not-so-distant future of compact, field-deployable, quantum products (such as computers, clocks, inertial sensors) will require cost-effective and mass-producible packages. Cold atom quantum technology is well-positioned to serve a wide variety of quantum applications, and advances in vacuum technology are enabling this cold atom quantum future. ColdQuanta strives to support the quantum ecosystem and cultivate a technology base that serves many emerging applications with a common underpinning technology, namely a compact cold atom UHV package: the Quantum Core. Advancing the Quantum Core will pave the way to diverse quantum products at scale. We will overview vacuum technology's crucial role in the quantum industry, dive into some specific technologies, and gaze into the future of commercialized Quantum Cores powering quantum products in diverse applications.

9:00am **VT-MoM-3 Non-Magnetic UHV Chambers and Feedthroughs for Quantum Applications: A Challenge for Vacuum, Optics and Mechanics*, Klaus Bergner,*** *J. Hertel, A. Trützschler, M. Flaemmich,* VACOM Vakuum Komponenten & Messtechnik GmbH, Germany

Quantum technology is currently experiencing a huge push towards commercialization. This means that basic experiments are more and more transferred into industrial applications. This means that enabling technologies must meet new quality criteria. In particular, the interplay between vacuum technology, mechanical and optical requirements must be taken into account. Vacua in the UHV/XHV range have to be achieved and several optical access ports for different optical tools have to be positioned in the range of a few µm to each other and.

In order to fulfill all this demands efficiently, aluminum CF components offer the possibility of providing customized solutions with high geometrical accuracy, reduced weight, outgassing rates of 1E–14 mbar*l/s/cm² as well as non-magnetic properties.

The talk covers the design of non-monolithic and monolithic CF vacuum chambers made from aluminum by using AluVaC®-technology. By discussing customized chamber designs, the talk shows that a monolithic design leads to a paradigm shift, since a monolithic chamber can be designed much more compactly, manufactured faster and without welding seams.

In combination with different optical components, the talk addresses the UHV compatibility of AluVaC®-viewports as well as VACOM made optical feedthroughs. Thorough different tests prove the UHV suitability with low outgassing rates shine light on product-relevant changes under extreme conditions.

9:20am **VT-MoM-4 Comparison of Quantum and Classical Vacuum Standards*, Daniel Barker,*** *N. Klimov, E. Tiesinga, J. Fedchak, J. Scherschligt, S. Eckel,* National Institute of Standards and Technology

We present a comparison of NIST's cold atom primary vacuum standard and a dynamic expansion vacuum standard. The cold atom vacuum standard (CAVS) converts the background-gas-induced loss rate of atoms from a magnetic trap into vacuum pressure using atom-molecule collision cross-sections calculated from first-principles quantum scattering theory. An extreme-high-vacuum (XHV) flowmeter and dynamic expansion system generate low-uncertainty partial pressures within the CAVS atom trap. To validate the CAVS, we compare its measured pressure to the pressure set by the dynamic expansion vacuum standard. We will present comparisons using a variety of noble gases and common vacuum contaminant species colliding with two species of sensor atoms. Our results open the way to vacuum gauge calibrations in the XHV and deployable pressure sensors with embedded traceability.

9:40am **VT-MoM-5 Direct Comparison of Two Portable Cold Atom Vacuum Standards*, Stephen Eckel,*** National Institute of Standards and Technology (NIST)*; L. Ehinger,* Seattle University*; D. Barker, J. Fedchak, J. Scherschligt,* National Institute of Standards and Technology (NIST)

We demonstrate the operation of the portable cold atom vacuum standard (pCAVS) by directly measuring the same vacuum with two independent devices. The pCAVS, designed as a replacement to the Bayard-Alpert ionization gauge, measures the loss rate of atoms from a magnetic trap, and converts that loss rate into a vacuum pressure using *ab initio* quantum-scattering calculations. Our pCAVS devices share the same laser system. Loss rate measurements are interlaced between the two, allowing for simultaneous readout. When initially assembled, the two pCAVS together detected a leak on the order of 10^{-6} Pa L/s. After fixing the leak, the two pCAVS measured the same pressure of 41.8 nPa with approximately 2 % uncertainty. Operation of the pCAVS was found to cause some additional outgassing in the vacuum, raising the base pressure approximately 1 nPa. With improved thermal management and better modeling of other loss mechanisms, we expect that the uncertainty can be decreased sufficiently to allow primary pressure measurements in the extreme-high-vacuum range (< 10^{-9} Pa).

10:00am **VT-MoM-6 Reference Ionization Vacuum Gauge*, Martin Wüest,*** *F. Scuderi,* INFICON Ltd., Liechtenstein*; J. Šetina,* Institute of Metals and Technology, Slovenia*; K. Jousten, M. Bernien,* Physikalisch-Technische Bundesanstalt - Berlin, Germany*; C. Illgen,* Physikalisch-Technische Bundesanstalt - Berlin, Germany*; N. Bundaleski,* Nova School of Sciences and Technology, CEFITEC, Portugal*; B. Jenninger, A. Stöltzel,* CERN, Switzerland

In the framework of the EURAMET project 16NRM05 a novel ionization gauge was developed. The goal was to develop a stable gauge suitable as a reference standard in the high vacuum range. A robust design eliminates many of the weak points of present day Bayard-Alpert gauges. Results of performed measurements show sensitivity spread within an interval ± 1.5 % at 95 % confidence level. Due to its simple geometry, sensitivity values can in principle be computed for any gas with a known ionization cross section. Known and stable relative sensitivity factors are important properties for the calibration of mass spectrometers. We will present some aspects of the gauge design and performance in conjunction with an associated controller.

10:40am **VT-MoM-8 Towards an Ionization Vacuum Gauge Suitable as a Reference Standard*, Nenad Bundaleski,*** CEFITEC, NOVA School of Science and Technology (FCT-NOVA), NOVA University Lisbon, Portugal **INVITED**

Ionisation vacuum gauges are the only pressure measurement devices covering a pressure range from high vacuum down to extremely high vacuum. However, these instruments lack precision, accuracy and stability, which is a misfortunate fact knowing the importance of these pressure ranges in both science and high technologies. Calibration of mass spectrometers and measurement of pumping speeds are examples of tasks that are particularly vulnerable in that respect. There are two major sources of problems with the operation of ionisation gauges: maintaining stable path lengths of primary electrons throughout the ionisation volume, and contribution of secondary particles emitted from electrodes (photons, electrons, ions and neutrals) to the pressure reading. These phenomena will be analysed in some detail in the frame of this talk, including the solutions applied in different available gauges to handle them. In the second part of the talk, we will present a design of a novel ionisation gauge recently developed for metrology applications in high vacuum, and discuss solutions aiming to suppress the above mentioned issues. However, the proposed design may potentially have problems with space charge effects, which limits its range of operation at the lowest pressures.

11:20am **VT-MoM-10 Evaluating low Pressure Resolution Limits for Optical Refractometry***, **Jacob Ricker**, K. Douglass, J. Hendricks,* National Institute of Standards and Technology (NIST)*; S. White, S. Syssoev,* MKS Instruments, Inc.

NIST with a collaboration research and development partnership with MKS Instruments has created a portable Fixed Length Optical Cavity (FLOC) pressure standard based on gas refractivity. The NIST team is now working to push the limits of pressure measurement into the UHV range. The goal for the new device would be to fill the gap in quantum-based traceability that currently exists between the FLOC and the Cold Atom Vacuum Standard, from 1 Pa to 10^{-5} Pa. To achieve the measurement goals, several sources of noise and drift need to be studied and eliminated. The desired sensitivity requires a frequency measurement (heterodyne signal between two 194 THz cavities) to have noise on the order of 1 Hz. To achieve this, the portable FLOC must be redesigned with state-of-the-art lasers and cavity mirrors, vibration isolation, and improved thermal control. The current FLOC low pressure performance will be estimated and initial testing results along with our proposed pathway to ultra-high vacuum measurements will be presented.

11:40am **VT-MoM-11 Vacuum Fixed Length Optical Cavity (VFLOC): Optical Pressure Measurements Approaching Ultra-High Vacuum***, **Kevin Douglass**, J. Ricker, J. Hendricks,* NIST

With the goals of achieving quantum traceability over a broad pressure scale NIST is developing a Vacuum Fixed Length Optical Cavity (VFLOC) that will have a base pressure in the ultra-high vacuum range.The current FLOC operates in the 1 kPa to 150 kPa pressure range and the Cold Atom Vacuum Standard (CAVS) has an upper limit near 10^{-5} Pa.The main limitation for pressure resolution and ultimate base pressure is the fractional frequency stability or frequency noise of dual cavity heterodyne signal.For operation at 1542 nm, hertz level frequency noise is required for achieving pressure noise floor on the order of 10^{-6} Pa (10^{-8} Torr).We will discuss current system status, design and recent results.

2D Materials Technical Group
Room 303 - Session 2D+AS+SS-MoA

2D Materials: Defects, Dopants, Edges, Functionalization, and Intercalation

Moderators: Chih-Kang (Ken) Shih, University of Texas at Austin, **Young-Woo Son**, Korea Institute for Advanced Study, Republic of Korea

2:20pm **2D+AS+SS-MoA-3 Effect of Defects in 2D Materials on the Dielectric Breakdown***, **Abdulrahman H. Basher**, M. Lanza, U. Schwingenschlogl,* King Abdullah University of Science and Technology (KAUST), Saudi Arabia

Two-dimensional (2D) materials are one of today’s hot topics in the semiconductor industry due to the fact that they can be used to fabricate nanodevices with attractive properties [1, 2]. However, they may lose their features in the presence of defects. For instance, 2D hexagonal boron nitride (hBN) is an excellent insulator but defects lower its breakdown voltage in the experiment [3]. Therefore, the aim of this study is to understand the mechanism of the dielectric breakdown in hBN as compared to amorphous boron nitride (aBN), using first-principles calculations based on density functional theory. The CP2K quantum chemistry and solid-state physics software package is used (quickstep algorithm based on the Gaussian and plane waves method) [4, 5]. The generalized gradient approximation of Perdew-Burke-Ernzerhof [6] is employed, and Grimme's dispersion correction [7, 8] with Becke-Johnson damping [9] is used as the van der Waals forces play a significant role in 2D materials. The obtained densities of states show that the size of the band gap decreases for increasing defect density, confirming that 2D materials are sensitive to defects. We explain the experimental observation that the breakdown voltage decreases from hBN (crystalline) to aBN (amorphous).

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2:40pm **2D+AS+SS-MoA-4 Palladium Nucleation and Alloying at the WTe$_2$(001) Surface***, **Prescott E. Evans**, P. Sushko, Z. Dohnálek,* Physical and Computational Sciences Directorate and Institute for Interfacial Catalysis, Pacific Northwest National Laboratory

A deeper understanding of atomic-scale functionalization of transition metal dichalcogenides, especially topologically interesting variants such as WTe$_2$, is critical in developing deployable structures in quantum information science. Discerning the role of intrinsic surface defects as adsorption and functionalization sites is a key step towards device realization. In this study, scanning tunneling microscopy (STM), X-ray photoemission spectroscopy (XPS), and density functional theory (DFT) were utilized to examine the initial nucleation and growth of palladium on the WTe$_2$(001) surface as both a function of coverage and temperature. XPS measurements of the WTe$_2$(001) surface after palladium deposition at room temperature show significant interaction between Pd and surface tellurium reminiscent of PdTe$_2$ in electronic structure with an absence of interaction between Pd and tungsten. Using STM, we found palladium deposited at room temperature, where Pd clusters outnumber surface defects more than 10:1, produced no change in surface defect density. This indicates a lack of interactions between deposited Pd clusters with intrinsic surface defects. The annealing temperature-dependent STM studies further show that palladium clusters are stable to about 475 K. Palladium deposition at an elevated temperature of 425 K was performed to determine that the lack of nucleation on defects is, in fact, not a result of diffusion limitations during the growth. Complementary theoretical studies predict that palladium atoms interact strongly with Te adatoms and Te vacancies, while only binding weakly on pristine WTe$_2$(001). Based on these results, we conclude that the nucleation of Pd clusters is initiated by mobile Te adatoms that likely significantly outnumber other surface defects. Our high-temperature Pd deposition studies further support this assertion. Atomically resolved images of large Pd nanoparticles annealed above 475 K exhibit a superstructure on the top terrace indicating alloying with tellurium. Atomically precise, tailored heterostructures with tunable electronic, and topological properties are necessary for the growing need for quantum devices. A full account of the surfaces of these quantum materials, as in with WTe$_2$(001) where excess chalcogenide complicate interactions at the surface, is vital in directing both accurate predictive theory and material synthesis efforts.

3:00pm **2D+AS+SS-MoA-5 Advanced Doping Schemes for 2D Nb:WS$_2$ for Catalysis and Electronics***, **Jeff Schulpen**, C. Lam, W. Kessels, M. Verheijen,* Eindhoven University of Technology, The Netherlands*; A. Bol,* University of Michigan, Ann Arbor

Two-dimensional semiconductors such as WS$_2$ are promising materials for use in next-generation nanoelectronics due to their high mobility and scalability allowing for ultra-short gates. Doping is required to make the p-type FETs needed for CMOS logic and doping can also reduce the contact resistance, which is another important challenge to overcome for transistors based on 2D materials.[1] Separately, doped 2D materials are receiving interest as affordable catalysts, as the dopants enhance the catalytic activity of the basal plane in addition to the already high activity of the edge sites.[2]

Essential for both electronic and catalytic applications is the precise control over the amount and distribution of dopants in the film. The synthesis method of atomic layer deposition (ALD) allows excellent control over these parameters such that e.g. graded doping profiles and edge decorations can be achieved.[3]

In this work we synthesize Nb-doped WS$_2$ by plasma-ALD and characterize the electronic and catalytic performance of the films.Conventional supercycles of type (AC)$_m$(BC)$_n$ were used to achieve excellent composition control from W-rich to Nb-rich films. Optimal hydrogen evolution reaction (HER) activity was found for Nb-rich films (~85% Nb). Beyond composition tuning, we investigate the effect of different edge terminations on the HER activity by modifying the cycle order in the ALD process. For electronic applications where low dopant concentrations are relevant, we use a modified (AC)$_m$(ABC)$_n$ scheme, where adsorbed W precursor largely inhibits adsorption of the Nb precursor. This allows for better dopant distribution than conventional supercycles, thereby improving the resistivity and Hall mobility of the films by a factor of two. Further characterization of devices based on the grown films is presented.

These results confirm that ALD-grown Nb-doped WS$_2$ is a promising material for both electronics and catalysis, and that the use of advanced doping schemes can further improve the performance of these films. This also serves as a demonstration of inhibition-assisted doping using ALD, which could be of interest for other material systems.

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2. Tang, L. *et al. Adv. Funct. Mater.***31**, 2006941 (2021).
3. Schulpen, J. J. P. M. *et al. 2D Mater.***9**, 025016 (2022).

4:00pm **2D+AS+SS-MoA-8 Atomic Imaging of Dynamic Behaviour at 2D Material Solid-Solid and Solid-Liquid Interfaces***, **Sarah Haigh**,* University of Manchester, UK **INVITED**

Transmission electron microscopy (TEM) is used for understanding the local structure of nanomaterials. Although, we are frequently concerned about understanding behaviour during chemical reactions or while undergoing physical processes, most TEM is performed with the sample exposed to high vacuum, which can change the atomic structure of surfaces and interfaces. Unfortunately, commercial in-situ liquid, gas or electrochemical cell TEM imaging holders often severely limit atomic resolution imaging and chemical analysis.

For investigating the chemical reactivity and degradation of 2D materials without exposing them to the TEM vacuum, an effective approach is to encapsulate the sample between two inert and impermeable few-layer 2D sheets (such as graphene or hexagonal boron nitride). This also enables transfer of air sensitive specimens from an inert vacuum or glove environment to the TEM without exposing the material to atmospheric conditions. We have applied this approach to study air sensitive 2D materials, including local point defects, doping and edge structures in a wide range of structures (e.g. CrBr3, GaSe, black phosphorus) (Fig. 1c)[1,2]. We also find that encapsulation with inert 2D materials is an effective route to preserve the delicate surface structure of hydrated 2D materials, enabling the visualization of exchangeable surface cations on few layer clays and micas [3] and a route to understand the changes in atom/ion motion at interfaces where the 2D materials are twisted with respect to each other (Fig. 1d).[3,4]

This 2D heterostructure approach can also be used to investigate solid-liquid interfaces. Building on nanochannel technology developed by the group of Andre Geim (Fig. 1b)[5] we have developed in-situ liquid phase TEM imaging using 2D heterostructure nanochannels. The in-situ 2D heterostructure liquid cell approach provides atomic resolution imaging and analysis and makes it possible to study the earliest stage of chemical synthesis [6]. It also reveals the large differences in adatom adsorption sites on 2D surfaces in vacuum compared to hydrated environments and allows study of dynamic adatom motion at solid liquid interfaces [7]; something that was not previously possible by any technique (Fig. 1a).

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4:40pm **2D+AS+SS-MoA-10 Electrodeposition of Nanofiberous H-Type MnO_2 Birnessite on Epitaxial Graphene Silicon Carbide Heterostructures, and transformation to Alkali Birnessites (Na, Li, K) via Simple Intercalation***, **Michael Pedowitz**, D. Lewis, K. Daniels,* University of Maryland, College Park

Mixed valence manganese oxides (MnO_x) have attracted significant research interest in recent years due to the reversible low energy redox reactions between manganese oxidation states (Mn^{+2}, Mn^{+3}, and Mn^{+4})[1], which has enabled its use in catalysis[2], energy storage[3], and gas sensing[4]. Of these manganese oxide compounds, manganese dioxide (MnO_2) has been of particular interest due to its wide variety of synthesized structural polymorphs (α (1x2 tunnel), β (1x1 tunnel), γ (spinel), and δ (layered))[5] which allow for significant control over the active surface area and reactive properties MnO_2. In particular, the Mn^{+3} defect density, which has been found to increase the reactivity of the MnO_2 film[6], is highly variable between polymorphs, with the δ phase exhibiting the highest defect density. Water stabilized δ-MnO_2 (H-δ-MnO_2) in particular contains the highest number of Mn^{+3} defects due to the presence of $Mn^{+2/+3}$ in the interlayer, which neutralize the layer charge from lattice defects[7]. However, the production of H-δ-MnO_2 has proven challenging in the literature. In this work, we present the synthesis of H-δ-MnO_2 on epitaxial graphene silicon carbide via electrodeposition. The electrodeposition was carried out in a 3 electrode electrochemical cell in a 3-step process with a duration of 1.25 seconds. The resulting films were then characterized using a combination of Raman spectroscopy, atomic force microscopy (AFM), and scanning electron microscopy (SEM) to confirm the formation of H-δ-MnO_2 and probe its surface morphology. The Raman spectra indicated the successful formation of H-δ-MnO_2, while the AFM and SEM indicated the surface has a nanofibrous character, increases the active surface area of the thin film. We then demonstrated that the material can be converted to Alkali type (Li, Na, K) δ-MnO_2 via intercalation without damaging the EG substrate. After the process, the material was characterized again with Raman, AFM, and SEM, which confirmed the transformation from H-type to Alkali-Type. As the interlayer spacing of δ-MnO_2 and its applications are related to the intercalated ions, this demonstrates the tunability of this heterostructure and its potential to be a platform for a variety of applications, including energy storage and gas sensing.

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5:00pm **2D+AS+SS-MoA-11 Signature of Coexistence of Ferroelectricity and Ferromagnetism in a Quantum Material***, **I-Hsuan Kao**, S. Yuan, J. Katoch, S. Singh,* Carnegie Mellon University

Electric field-controlled magnetism by combining van der Waals (vdW) based semiconducting ferromagnets and Weyl semimetal is appealing because of the gate tunability and efficient charge-spin transduction[1], which can be exploited for modular memory and logic devices. Ferroelectric switching has been previously demonstrated in bilayer and trilayer WTe_2[2-4], where the polarity can be controlled by electric gating. VdW based semiconducting FMs, such as $Cr_2Ge_2Te_6$ (CGT), provide the opportunity to study tunable magnetic phenomena and to build superlattices with other quantum materials[5]. By coupling a semiconducting ferromagnet to a Weyl semimetal, magnetization can be induced at the interface by magnetic proximity effect. We have fabricated WTe_2/CGT devices and observed anomalous Hall effect, which is a signature of magnetic proximity effect. In the same device, we are able to perform ferroelectric switching of WTe_2 by applying an electric field. Furthermore, the presence of the anomalous Hall effect can be enhanced (suppressed) by negative (positive) electric gating. We will present detailed measurements, which are required to understand this novel platform where ferroelectricity and ferromagnetism coexist.

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Atomic Scale Processing Focus Topic
Room 317 - Session AP+AS+EL+MS+SS-MoA

Advancing Metrology and Characterization to Enable Atomic Scale Processing

Moderators: Steven M. George, University of Colorado at Boulder, **Rudy Wojteki**, IBM Almaden Research Center

1:40pm **AP+AS+EL+MS+SS-MoA-1 Nanoscale Chemical Analysis and Mapping of Atomic and Molecular Scale Processes via Infrared Photo-Induced Force Microscopy***, **Sung Park**,* Molecular Vista **INVITED**

As semiconductor device feature sizes move beyond the sub-7 nm technology node, atomic scale processing techniques such as atomic layer deposition (ALD) and atomic layer etching (ALE) are being adopted to gain control over key processing parameters.These techniques are commonly combined with thin polymer barrier layers such as self-assembled monolayers (SAM) that are selectively located to achieve area selective deposition or etching. In protein and DNA chips, monolayers of specific molecules are engineered and patterned to guide the target molecules to specific locations.Common to these devices and processes are the atomic scale thicknesses, nanoscale lateral dimensions, and the combination of multiple materials consisting of organic and inorganic compounds, metals, and 1D/2D materials which demand new metrology and characterization techniques to assess and monitor these advanced processing techniques.Photo-induced Force Microscopy (PiFM) [1] combines infrared (IR) absorption spectroscopy and atomic force microscopy (AFM) to achieve nanoscale chemical analysis via localized IR absorption spectrum and mapping of heterogeneous materials on the surface of a sample (with sub-5 nm spatial resolution).The spectroscopic capability is useful for ascertaining the presence and quality of the molecular species. The mapping capability is useful for investigating surface functionalization and chemical pre-patterns as well as selectively deposited materials in area-selective processes like block copolymer directed self-assembly, sequential infiltration synthesis, and a variety of area-selective deposition techniques. PiFM applications on various atomic and molecular scale processes will be presented.

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2:20pm **AP+AS+EL+MS+SS-MoA-3 Area-Selective Deposition/Patterning of Boron Carbide Layers: Etch Studies***, **Raja Sekhar Bale**, R. Thapa, A. Caruso,* University of Missouri-Kansas City*; J. Bielefeld, S. King,* Intel Corporation*; M. Paquette,* University of Missouri-Kansas City

The semiconductor industry is pushing the boundaries of device scaling by way of novel processing methods and increasingly complex patterning schemes. This requires a variety of functional and patterning-assist materials as well as advanced deposition techniques. For years, silicon-based materials have been used to meet these needs; however, these alone cannot fulfill the range of material requirements moving forward. Boron carbide has shown promise due to its compelling dielectric, thermal, mechanical, chemical, and etch properties. Toward applying this material to next-generation integration schemes, we have been exploring the potential of going beyond traditional growth processes (e.g., plasma-enhanced chemical vapor deposition) and investigating innovative area-selective atomic layer deposition (AS-ALD) strategies. Herein we explore schemes for the selective dielectric on metal/dielectric deposition of boron carbide using monolayer and layer-by-layer methods. In particular, we focus on etch studies (wet and dry) toward understanding the stability and removal of these layers. X-ray photoemission spectroscopy (XPS), scanning electron microscopy (SEM), and atomic force microscopy (AFM) techniques are employed for the characterization and imaging of the resulting surfaces.

2:40pm **AP+AS+EL+MS+SS-MoA-4 Smoothing of Surfaces by Atomic Layer Deposition and Etching**, *S. Gerritsen, N. Chittock, V. Vandalon, M. Verheijen,* Eindhoven University of Technology, The Netherlands; *H. Knoops,* Oxford Instruments Plasma Technology, Netherlands; *E. Kessels, **Adrie Mackus**,* Eindhoven University of Technology, The Netherlands

With critical dimensions scaled down to the nanoscale in current electronics, surface and interface roughness increasingly limit device performance. In this work, we use simulations and experiments to explore whether atomic layer deposition (ALD), atomic layer etching (ALE) and combinations of these techniques can be used to smoothen surfaces, while processing materials with excellent uniformity and atomic scale control. The smoothing is experimentally demonstrated by atomic force microscopy and transmission electron microscopy analysis.

Many previous studies have shown that ALD and ALE can smoothen surfaces,[1,2] but the extent of smoothing has not been systematically characterized and the mechanisms of smoothing are only partly understood. In our studies, finite difference simulations were performed that describe ALD/ALE as a uniform front from which the deposition/etching propagates isotropically at every point. Al_2O_3 ALD experiments using TMA and O_2 plasma validated this uniform front propagation model. A smoothing rate of $5.5\cdot10^{-3}$ nm RMS roughness reduction per nm of deposition was determined, revealing that significant smoothing by ALD requires relatively thick films (e.g. > 20 nm).

Al_2O_3 ALE from TMA and SF_6 plasma[3] resulted in a larger roughness reduction of $9.8\cdot10^{-3}$ nm/nm, which is explained by considering that the fluorination of the surface depends on the local curvature, such that peaks are smoothed more than valleys. In other words, for ALE two mechanisms contribute to the smoothing, i.e. uniform front propagation and curvature-dependent fluorination. In order to benefit from the enhanced smoothing by ALE, especially combinations of ALD and ALE in supercycle recipes can be very effective in smoothing surfaces, as will be highlighted in the contribution.

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3:00pm **AP+AS+EL+MS+SS-MoA-5 Thermal Atomic Layer Etching of Amorphous Aluminum Nitride Using Sf$_6$ Plasma and Al(Ch$_3$)$_3$**, ***Haozhe Wang**, A. Houssain, D. Catherall, A. Minnich,* California Institute of Technology

We report the thermal atomic layer etching (ALE) of amorphous aluminum nitride using sequential exposures of low-power SF_6 plasma and trimethylaluminum ($Al(CH_3)_3$, TMA). ALE was observed at temperatures greater than 200 °C, with etch rates varying with temperature from 0.1 Å/cycle at 200 °C to 1.9 Å/cycle at 300 °C, as measured using ex-situ ellipsometry. The self-limiting nature of the reactions was established by verifying that no etching occurred with only SF_6 or TMA. The etched surface was characterized using atomic force microscopy and x-ray photoemission spectroscopy. After 50 cycles of ALE, the etched surface was found to contain a lower concentration of oxygen compared to the original surface and exhibited a~35% decrease in surface roughness. These findings have relevance for applications of AlN in nonlinear photonics and semiconductor devices.

3:20pm **AP+AS+EL+MS+SS-MoA-6 Thermal Atomic Layer Etching using MoF6-H2O precursors**, ***Anil Mane**, J. Elam,* Argonne National Laboratory, USA

Well controlled atomic layer etching (ALE) processing is needed for the creation of next generation complex 3D devices. A simple semiconductor processing compatible thermal ALE method is preferred for the process integration point of view. Recently we have developed the MoF6-H2O precursors based etching methods for the etching of atomic layer deposited (ALD) TiO2, Ta2O5 and MoS2 in a precise controlled manner. The etch rate and etch behavior of these materials mainly controlled by processing temperature (100-325^{o}C) and precursors dose times. The MoF6-H2O etching process of these ALD grown TiO2, Ta2O5 and MoS2 was studied by in-situ methods such as infrared spectroscopy (FTIR), quartz crystal microbalance (QCM), and spectroscopic ellipsometry (SE). Additionally, at present we have also developed novel in-situ calorimetry method to measure chemical reaction heat in ALE precursor's reaction. Here some of latest results on this in-situ ALE-calorimetry method will also be presented.

4:00pm **AP+AS+EL+MS+SS-MoA-8 The Thinner, the Better - Characterization of Ultra-Thin Films by Low Energy Ion Scattering (Leis)**, ***Thomas Grehl**,* IONTOF GmbH, Germany **INVITED**

Current and future thin film processes require quantitative characterization from the early phases of film growth to complex film stacks with a total thickness of only a few nm. While many surface analytical techniques are challenged by this requirement, Low Energy Ion Scattering (LEIS) analysis is ideally suited for ultra-thin film and sub-monolayer characterization. The key property is its single atomic layer information depth.

By scattering noble gas ions from the surface of the sample, LEIS determines the elemental composition of the surface of the outermost atomic layer. Nucleation processes and layer closure are investigated, but also diffusion from the bulk towards the surface can be studied with in-situ sample heating and continuous monitoring of the surface composition.

In addition to the surface composition, also the distribution of elements over the first few nm of the sample is contained in the spectra. The so-called "in-depth information" is acquired in a virtually non-destructive way, avoiding sputtering and therefore the long measurement times and artefacts associated with it. For sufficiently thin films, the depth resolution is only a few Å. This allows to study the development of the film thickness while also monitoring film closure to determine the growth mode.

In some cases, low energy noble gas sputtering is applied to extend the depth range beyond a few nm or to handle complex materials where "in-depth" and surface information cannot be deconvoluted.

In this contribution, we will highlight a number of examples from quite different materials and film systems. These will be used to illustrate how LEIS is applied in practical way. We will show how LEIS contributes unique information for modern ultra-thin film characterization.

4:40pm **AP+AS+EL+MS+SS-MoA-10 Intrinsic Area Selective Atomic Layer Deposition of MoS$_2$ Thin Films**, *J. Soares, **Wesley Jen**, S. Hues,* Boise State University; *J. Wensel,* Micron Technology Inc; *E. Graugnard,* Boise State University

As the critical dimensions in today's semiconductor devices continues to shrink, new methods for device fabrication are paramount for continued reduction in scaling. These fabrication processes must be adaptable in order to evolve with future technology nodes and scales, while providing flexible material integration techniques within the high complexity of device structures. Area selective atomic layer deposition (ASALD) is a deposition technique that utilizes a bottom-up patterning approach for self-alignment of deposited materials. ASALD operates on the basis that functional groups either present or absent on a growth surface will promote or inhibit nucleation. This contrast can lead to selective deposition. In addition to compatible processing techniques, next generation materials also need to be studied. Layered two-dimensional (2D) molybdenum disulfide (MoS_2) is a semiconducting material that shows great promise due to its atomically thin structure and impressive electrical properties. In this work, we report the ASALD of MoS_2 on patterned template substrates of common dielectric materials versus thermal silicon oxide and nitride. Growth and non-growth surfaces were initially screened with X-ray photoelectron spectroscopy (XPS) characterization of blanket MoS_2 films after numerous ALD cycles. The selectivity parameter between surfaces was calculated using XPS, revealing a high selectivity of S = 0.94 after 20 ALD cycles for growth on ALD alumina versus thermal silicon oxide. These results identified contrasting surfaces that were then patterned to investigate area selectivity. MoS_2 ALD was performed at 200 °C on patterned surfaces that were then annealed at 650 °C for 30 minutes. Samples were characterized using Raman spectroscopy maps of crystalline MoS_2 modes and time-of-flight-secondary ion mass spectroscopy (ToF-SIMS) elemental mapping, which confirmed ASALD. These results hold promise for advancing the integration of 2D materials into device manufacturing.

5:00pm **AP+AS+EL+MS+SS-MoA-11 In Situ Measurements of Surface and Film Stress during Atomic Layer Deposition of Al_2O_3 and AlF_3 using Wafer Curvature Techniques***, **Ryan B. Vanfleet**, E. Sorinto, A. Cavanagh, V. Bright, S. George,* University of Colorado at Boulder

In situ surface and film stress were measured during atomic layer deposition (ALD) using wafer curvature techniques in a new custom reactor. Aluminum oxide (Al_2O_3) ALD using trimethylaluminum (TMA) and H_2O as the reactants was used as a model system to test this new apparatus. Al_2O_3 ALD was explored at different deposition temperatures ranging from 130 to 285°C. The in situ measured film stress during Al_2O_3 ALD is a tensile stress of 450 MPa at 130°C (Figure 1). The tensile stress then decreases with increasing deposition temperature. These in situ temperature-dependent Al_2O_3 ALD film stresses are in good agreement with ex situ film stress measurements for Al_2O_3 ALD films reported in the literature [1].

High sensitivity wafer curvature measurements are also able to measure the surface stress from individual surface reactions (Figure 2). These in situ measurements revealed that the TMA exposure results in a compressive surface stress. This compressive stress is attributed to repulsion between surface methyl species. In addition, the H_2O exposure removes surface methyl species and releases the compressive stress. The compressive surface stress resulting from the TMA exposure grows from 0.4 N/m at 150°C to 0.75 N/m at 285°C. This increase in the compressive surface stress from the TMA exposure can be attributed to the greater relative change in methyl coverage at higher deposition temperatures.

Additional in situ measurements have explored the surface and film stresses during AlF_3 ALD using TMA and HF as the reactants. AlF_3 ALD showed similar surface stress behavior to Al_2O_3 ALD. The TMA exposure again results in a compressive stress attributed to repulsion between surface methyl groups. The HF exposure then removes the methyl groups and releases the compressive stress. At AlF_3 ALD temperatures between 150-200°C, the compressive surface stress resulting from the TMA exposures is ~0.45 N/m. In marked contrast to Al_2O_3 ALD, AlF_3 ALD displayed no film stress during film growth. This lack of film stress in AlF_3 ALD films may be related to the nature of the AlF_3 ALD film as a molecular solid.

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Applied Surface Science Division
Room 320 - Session AS+CA+EL+EM+LS+SE+SS-MoA

Quantitative Surface Analysis

Moderators: Jordan Lerach, PPG Industries, **Hong Piao**, FUJIFILM Electronic Materials USA., Inc.

1:40pm **AS+CA+EL+EM+LS+SE+SS-MoA-1 Hard Targets: Developing Tools for Quantitative HAXPES***, **David Cant**,* National Physical Laboratory, UK **INVITED**

'Soft' x-ray based XPS, using aluminium or magnesium anodes, has been a workhorse of surface analysis labs for decades. Over this time, substantial efforts have been made in the development of tools such as sensitivity factors, transmission function corrections, physical parameter databases, simulation software, interpretation methods, and more. Thanks to the existence of such tools, the data obtained from 'soft' XPS, with careful analysis, can provide a strong, quantitative understanding of samples in terms of the relative concentration of elements and their chemistry within the topmost ~10 nm of material. Nevertheless, sometimes 10 nm is not enough.

Until recently, XPS of materials beyond this topmost region of the surface would require either destructive depth profiling of the sample or the use of synchrotron light sources; the former carries its own metrological challenges, as well as ruining a sample, while the latter introduces a plethora of complexities which render calibration difficult. However, recent developments in the design of instruments utilising higher-energy x-ray anodes have begun to make HAXPES instruments more readily available in the lab. This allows far more analysis of samples that previously might have been restricted to synchrotron studies; for example in non-destructive depth-profiling of coated samples with overlayers beyond the ~10 nm limit of 'soft' XPS. Yet with new instruments come new issues; transmission function calibrations that work for the 0 - 1400 eV energy range are not much use for spectra that stretch some KeV beyond, and relative sensitivity factors for each new photon energy and instrument geometry are needed, particularly given the cornucopia of new core levels made available, and the breadth of sensitivity at higher photon energies.

Here we discuss progress towards more quantifiable XPS and HAXPES measurements. A method for the calculation of theoretical sensitivity factors is described, applicable to instruments of any geometry for x-ray sources in the energy range 1.5 - 10 keV, and their validity for depth-profiling of samples well beyond the depths achieved by aluminium sources is demonstrated. We discuss developments in straightforward transmission-function calibrations of standard aluminium sources by the use of a mathematically-defined reference spectrum, as well as progress towards transmission calibration of higher energy sources for which reference spectra do not yet exist. From these developments, the possibility of a 'universal' calibration and sensitivity scheme for both lab- and synchrotron-based HAXPES systems at a range of energies is proposed.

2:20pm **AS+CA+EL+EM+LS+SE+SS-MoA-3 Process-Induced Reactions in Interfaces of High-K/Metal Gate Stacks Studied Using HAXPES***, **Thierry Conard**, A. Vanleenhove, F. Mascarenhas, I. Hoflijk, I. Vaesen,* IMEC, Belgium

While high-energy photoemission has been in use for decades, it has remained mostly confined to synchrotron radiation facilities. Synchrotron beamlines allow a large flexibility regarding measurement conditions and set-up but are inconvenient in the framework of technological developments, where routine analysis of material systems is needed. The recent availability of performant lab-scale high-energy photoemission spectrometers [1,2,3] alleviate these beamline limitations and thus allow to investigate technological relevant models.

In this presentation, we will demonstrate the potential of HAXPES lab-scale systems regarding application in the semiconductor industry, and more specifically regarding the chemical analysis of interfaces. We will demonstrate the investigation of modifications in layer chemistry of buried layers in multi-layer high-k/metal gate stacks upon thermal treatments. Annealing is one of the critical stages during manufacturing of gate stacks and chemical modification at interfaces play a major role in device performance. With this presentation we will present results on simple stacks such as $TiN/HfO_2/SiO_2/Si$ as well as more complex stacks such as $TaN/TiAl/TiN/HfO_2/SiO_2/Si$ or $W/TiN/HfO_2/SiO_2/Si$. Results will be presented obtained both with Cr Kα (5.4 keV) and Ga Kα (9.25 keV) HAXPES. The respective advantages of these two energies will be discussed in terms of chemical identification, sensitivity and quantification.

Acknowledgement

We are grateful to the Research Foundation Flanders (FWO) for funding the HAXPES Lab instrument within the HERCULES program for Large Research Infrastructure of the Flemish government. Project I014018N.

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2:40pm **AS+CA+EL+EM+LS+SE+SS-MoA-4 Quantification and Reporting of XPS Data Taken Under Near Ambient Pressure Conditions – Chances and Challenges in Acquision Speed, Beam Damage, Sensitivity, Reliability, Reproducibility and Repeatability***, P. Dietrich, **Andreas Thissen**,* SPECS Surface Nano Analysis GmbH, Germany

Over the last fifty years significant developments have been done in photoelectron spectroscopy instrumentation and thus opened new fields of application. Especially XPS or ESCA developed into a standard analytical method in many labs for surface and material characterization. The number of users and the number of publications using XPS data has tremendously increased. But as a side effect it is a challenge to keep the level of knowledge about the method and correct data interpretation at a high level for all users of these data.

To avoid errors in the interpretation of XPS data instrument manufacturers put efforts inside their instruments and software packages to help and guide the user through data acquisition, data quantification and interpretation and finally also through data reporting. By this data can be made compatible with existing ISO and other community standards. But even more, data quality becomes transparent also in times of open source publications and open data repositories.

For the last ten years XPS under near ambient pressure conditions (NAP-XPS) has gained significant attention in the XPS community. The technique allows for standard analysis of samples under pressures up to about 50 mbar. This opens XPS to liquids, solid-liquid interfaces, gas-solid-interfaces, gas-liquid-interfaces. New fields like operando studies on electrochemical systems, corrosion experiments, analysis of food samples, but also studies of biological samples have been added to the XPS portfolio. The background gas pressure in such experiments is beneficial for the analysis of materials, because it avoids beam damages and degradation due to UHV conditions and also enables true non-destructive analysis of all types of degassing samples and insulators. On the other hand, the absorption of X-rays in the gas atmosphere, the emitted electrons from the gas molecules and inelastic electron scattering in the gas influences the spectral distribution of photoelectrons significantly strongly influencing elemental identification, quantification and detection sensitivity. This presentation summarizes the special challenges in the interpretation of NAP-XPS data and uses several reference samples (mostly published in Surface Science Spectra) from different fields of application. Basic concepts for identification and quantification of spectral features are demonstrated. Finally an outlook is presented how close NAP-XPS is to be a routine metrology technique.

3:00pm **AS+CA+EL+EM+LS+SE+SS-MoA-5 The Modern Spectrometer – Reliable, Repeatable and Relatable***, S. Coultas, J. Counsell,* Kratos Analytical Limited, UK*;* ***Christopher Moffitt****,* Kratos Analytical Inc.*; C. Blomfield,* Kratos Analytical Limited, UK

The outlook of the XPS community has changed significantly in the last decade. The technique has seen constant steady growth due to the rise in surface-based material research – energy storage and harvesting are two such disciplines. This growth of new first-time users needs to be considered, as does the way in which faculties manage centralised analytical facilities. This has led to a change in the philosophy of the workflow of an XPS spectrometer and how the user interacts with the “tool”. In this modern era of devolved data and non-expert users the spectrometer itself needs to be reliable, repeatable and relatable. Reliable – delivers on the promise, Repeatable – consistency with data acquisition and processing, Relatable – simple, easy-to-use, non-expert. This new philosophy creates new challenges for manufacturers who need to deliver the best spectrometer for this new market whilst at the same time maintaining the expectations and beliefs of the traditional analyst.

The discussion will focus on defining the issues of the current XPS outlook and providing practical, workable solutions. The following topics, when combined together, will illustrate the holistic design principles of a modern spectrometer: Simplified workflow, standard methods, automated routines, parameter logging, calibrated and up-to-date sensitivity factors, processing operators, data output and report generation.

3:20pm **AS+CA+EL+EM+LS+SE+SS-MoA-6 Modulation with Atomic Number of the Shirley Background of the Photoemission Spectra of Transition Metals***,* ***Alberto Herrera-Gomez****, D. Guzman-Bucio,* CINVESTAV-Queretaro, Mexico*; D. Cabrera-German, M. Mayorga-Garay, O. Cortazar-Martinez, J. Torres-Ochoa, A. Carmona-Carmona,* CINVESTAV-Unidad Queretaro, Mexico*; M. Gonzalez Reyna ,* UNAM-Mexico*; V. Crist,* XPS Library*; C. Ospina-Ocampo,* Cinvestav-Unidad Queretaro, Mexico

The 2*p* photoemission spectra of the first-row pure transition metals are similar enough to each other to display a meaningful progression, through the row, of the characteristics of the peaks and background [1]. The same goes for the 3*d* spectra of the second-row pure transition metals [2]. In addition, there are similarities between the behavior of the peak and background parameters of these two rows, such as the dependence of the intensity of the Shirley background with atomic number. The Shirley background is largest for the first column (3B column of the periodic table), decreases to a local minimum to then rise again to a local maximum on the seventh column (8B). The large value of the Shirley background for the first column elements is correlated with the large asymmetry of the main peak and the presence of strong intrinsic plasmons. This correlation might be due to a similar physical origin [3] The local maximum in the 8B column coincides with the maximum of permutations of the valence band, as previously pointed out by Castle and Salvi [4]. The physical mechanism of these phenomena will be discussed.

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4:00pm **AS+CA+EL+EM+LS+SE+SS-MoA-8 Thin Film Analysis by XPS: Quantitative Modeling of Sputtering and Depth Profile Data***,* ***Lev Gelb****, A. Walker,* University of Texas at Dallas

We present progress in the simutaneous quantitative extraction of both compositional profiles and sputtering parameters from XPS depth-profiles of multilayer films. Depth-profile data are routinely processed to provide “fractional composition vs ion dose” profiles, but such profiles suffer from significant drawbacks: they are constructed assuming that the sample is homogeneous in the probed region, which is not true near interfaces, and it is not normally possible to precisely convert between units of ion dose and depth.

Our approach is to first construct analytical models for both the sample structure and for the erosion process, and then to determine the model parameters (layer thicknesses, interfacial widths, material removal rates, etc.) most consistent with the observed apparent fractional composition profiles. This is done numerically, by comparing simulated and observed apparent composition profiles in a maximum-likelihood framework using an evolutionary optimization algorithm. The only required inputs to the calculation are the “fractional composition” profiles (above) and models for the inelastic mean free paths (IMFPs) for each tracked peak.

We demonstrate the basic idea by analysis of using synthetic data. The resolution of the extracted depth profiles improves when additional peaks are incorporated in the analysis. Small deficiencies in the structure or sputter model do not strongly affect the extracted compositional profiles, while errors in the IMFPs used have much larger effects. We then discuss promising results obtained from the analysis of experimental data from some well-characterized samples. Finally, we discuss improvements and extensions of this modeling/analysis framework. The sputtering model can be extended to include in-sample mixing and chemical reactions. The scheme can also be extended to use complete spectra as input.

4:20pm **AS+CA+EL+EM+LS+SE+SS-MoA-9 Understanding and Controlling Sample Degradation on Modern XPS Spectrometers***,* ***David Morgan****,* Cardiff University, UK

As XPS systems become ever more user-friendly, with “load-point-click-report” type automated analysis possible, the expertise in understanding samples, their handling and ultimately identifying and dealing with experimental artefacts is slowly eroding.

It has been previously shown that developments in the charge compensation methodology employed, especially the use of dual electron-ion compensation systems, can cause significant damage to a range of inorganic and organic materials [1,2] and in some cases a synergistic effect from the x-rays on the degradation rates can be observed.

Herein, the degradation effect using x-rays and a dual beam neutraliser are explored and discussed, and a delineation of the effects from both neutraliser and the x-rays on a series of polymeric, organic and inorganic materials are presented, together with methodologies to mitigate, or at the very least minimise, such analysis induced damage and propose that which we believe to be a better way of estimating sample damage on a per-system basis than those previously published [3].

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4:40pm **AS+CA+EL+EM+LS+SE+SS-MoA-10 XPS Intensity Calibration and Validation Using Polyethylene and Ionic Liquids***, **Benjamen Reed,*** National Physical Laboratory (NPL), UK*; J. Radnik,* Bundesanstalt für Materialforschung und -prüfung (BAM), Germany*; A. Shard,* National Physical Laboratory (NPL), UK

For quantitative X-ray photoelectron spectroscopy (XPS) analysis, it is necessary to know the *energy-dependent spectrometer response function* ('transmission function') of the XPS instrument. There is a huge variability of transmission functions between different laboratories and instruments, as well as different acquisition parameters for the same instrument. For comparable and reproducible analyses, there is a necessity for a standardised method of intensity calibration and validation.

For intensity calibration, the simplicity of polyethylene's inelastic background can be described by a mathematical function that can be easily reproduced, is continuous, and noise-free. Instrument geometry must be considered due to the anisotropic emission of photoelectrons and the polarization of monochromated x-rays in many commercial XPS instruments. We therefore present geometry-corrected reference spectra of polyethylene for Al Kα instruments which are traceable to gold, silver, and copper reference spectra from the National Physical Laboratory (NPL). Polyethylene does not require in-situ sample preparation needing only to be scraped with a scalpel before measurement, making it a suitable method for instruments without an ion-sputtering source. VAMAS study A27 determined that over a kinetic energy range of 180 eV to 1500 eV, intensity calibration with polyethylene deviates by ±6.5% compared to previous NPL method using precious metals. Deviations less than 5%, and as low as 1%, are attainable with careful data acquisition from well-maintained instruments. This intensity calibration method is now being developed as an international standard under the auspices of ISO TC201 "Surface Chemical Analysis".

Once an instrument has been intensity corrected, it is good practice to validate the calibration by measuring a homogeneous sample of known composition. Ionic liquids have several notable properties that make them an ideal material for XPS analysis. Ionic liquids exhibit a high degree of lateral and depth homogeneity, are UHV compatible, and have well-defined stoichiometries. When deposited in recessed sample holder, the meniscus of an IL will be perfectly flat meaning that there are no contributions from sample topographic effects. 1-propyl-3-methyl-imidazolium-bis(trifluoromethyl sulfonyl)imide (Solapur®) is one such IL candidate, with core levels up to ~800 eV binding energy, making it apt for verifying the quantification of light elements, especially for organic materials. Here we present spectra for Solapur® ionic liquid and discuss how they may be used to validate an XPS intensity calibration.

Biomaterial Interfaces Division
Room 318 - Session BI+AS+HC+SS-MoA

Bioinspired Materials and Applications

Moderators: Sally M. McArthur, Deakin University, Australia, **Tobias Weidner**, Aarhus University, Denmark

1:40pm **BI+AS+HC+SS-MoA-1 Bioinspired Approaches to Prevent Microbes and Fouling on the Surface of Membranes***, R. Shah, T. Goodwin, **Jessica Schiffman,*** University of Massachusetts Amherst **INVITED**

The reliability and ease of operation of membrane-based water purification systems has led to their increased use in water and wastewater treatment. However, water and energy are mutually dependent critical resources; to produce clean water requires energy and the production of energy requires large volumes of water. Unfortunately, when microorganisms and other foulants accumulate on the surface of membranes and block their pores, more energy is required to operate the separation process even though its productivity is significantly reduced. The overall goal of this talk is to illustrate how bioinspired approaches can be used to enhance the properties of ultrafiltration membranes. Our first approach will demonstrate how we controlled the deposition of the bioinspired "glue" dopamine in order to fabricate ultrafiltration membranes with retained selectivity and pure water flux. Molecules for polymerization were immobilized on the membrane's surface yet prevented from attaching to the membrane's pores due to a backflow of nitrogen gas achieved using simple in-house constructed equipment. If time allows, I will provide an overview of our recent exploration into how pitcher plant inspired immobilized liquids can dramatically increase the fouling resistance of membranes that have consistent flux over at least ten cycles of operation. Biofouling during membrane-based operations is a major challenge and we suggest that there are numerous bioinspired approaches that can address this problem.

2:20pm **BI+AS+HC+SS-MoA-3 Antibiotic-Free Liquid Layers Decrease Bacterial Adhesion on Catheters In Vivo***, C. Fong,* University of Maine*; M. Andersen, A. Flores Mireles,* Notre Dame*; **Caitlin Howell,*** 5737 Jenness Hall

The rise of antibiotic resistance is one of the greatest global public health challenges of our time. Although new antibiotics continue to be discovered, the pace is slowing while the rate of discovery of new antibiotic-resistant organisms continue to grow at an alarming rate. New, non-chemical approaches are needed which can reduce bacterial surface attachment and growth without leading to further resistance. Over millions of years, Nature has developed several ways to mechanically direct or stop bacterial growth, leading to materials-based antibacterial mechanisms which are elegant, effective, and difficult for bacteria to overcome. One of these approaches, immobilized liquid layers, functions via the use of a mobile, dynamic, and sacrificial physical barrier between the bacteria and the surface which they may contaminate. *In vitro* proof-of-concept experiments using urinary catheters— one of the most common and infection-prone medical devices—liquid layers were found to reduce bacterial adhesion by 99% compared to untreated controls. In tests *in vivo*, the system performed beyond expectations, reducing not only bacterial adhesion but overall surface protein contamination as well. The results provide hope that continuing to engineer materials-based approaches to stop bacterial adhesion and growth can help us to stay ahead of antibiotic resistance.

2:40pm **BI+AS+HC+SS-MoA-4 Discovery of Cell Instructive Materials for Next Generation Medical Devices: Exploring Microtopography and 3D Shapes***, **Morgan Alexander,*** University of Nottingham, UK

The polymer biomaterials found in the clinic today are dominated by materials that have been chosen largely on the basis of their availability and mechanical properties. It would be desirable to design our way forward from this situation to new and better biomaterials chosen for positive interactions with surrounding cells and tissues. Unfortunately, our understanding of the interface between most materials and biology is poor. Only in isolated cases is there a good understanding of cell-material surface interactions and fewer still where material-tissue interactions are well characterised and understood.

This paucity of information on the mechanism of biomaterial interactions within the body acts as a roadblock to rational design. Consequently, we have taken a high throughput screening approach to discover new bio-instructive polymers from large chemical libraries of synthetic monomers presented as micro arrays. [1,2] This approach, akin to engineering serendipitous discovery, has resulted in novel materials which we have taken all the way from the lab to the clinic.

More recently we have extended our approach to explore the opportunities offered by micro topography and 3D shape manipulation to provide bio-instructive cues topography to immune cells, stromal cells and pathogenic bacterial cells. To do this we have developed and adopted a range of high throughput screening platforms, including theTopoChip[3], ChemoTopoChip [4] and used 3D printing to produce the ArchiChip [5]. The talk will focus on these topographic platforms and our findings, in particular novel topographies that reduce bacterial biofilm formation and provide beneficial host cell responses which has the potential to reduce infection in medical device implantation.[6]

References

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[2] Materials for stem cell factories of the future Celiz et al. **Nature Materials** 13 (6), 570-579 (2014).

[3] Immune modulation by design: using topography to control human monocyte attachment and macrophage differentiation Vassey et al. **Advanced Science** 7 (11), 1903392 (2020).

[4] Discovery of synergistic material-topography combinations to achieve immunomodulatory osteoinductive biomaterials using a novel in vitro screening method: The ChemoTopoChip Burroughs et al. **Biomaterials** 271, 120740 (2021).

[5] Innate Immune Cell Instruction Using Micron-scale 3D Objects of Varied Architecture and Polymer Chemistry: The ChemoArchiChip Vassey et al. under review.

[6] Micro topographical instruction of bacterial attachment, biofilm formation and in vivo host response Romero et al. under review.

3:00pm **BI+AS+HC+SS-MoA-5 Development of a Method for Visualizing Nanometer-Scale Three-Dimensional Structures of Chromosomes by Three-Dimensional Atomic Force Microscopy***, **Ryohei Kojima**, K. Miyazawa, K. Teramae,* Kanazawa University, Japan*; T. Sumikama,* PRESTO, JST, Japan*; M. Meguro,* Research Center for Experimental Modeling of Human Disease, Kanazawa University, Japan*; K. Imadate,* Osaka University, Japan*; N. Okano,* Kanazawa Unversity, Japan*; S. Horike,* Research Center for Experimental Modeling of Human Disease, Kanazawa University, Japan*; K. Hirahara,* Osaka University, Japan*; T. Fukuma,* Kanazawa University, Japan

Three-dimensional atomic force microscopy (3D-AFM) is capable of obtaining 3D force images at solid-fluid interface in sub-nanometer scale. In the previous research, 3D-AFM visualized molecular-scale hydration and flex molecular structures of bio samples such as lipid and DNA. As a next step, it is required to visualize 3D complex structures with high order molecular organizations.
In this research, we developed 3D-AFM for visualizing 3D folded structures of human chromosomes. Chromosome (Fig. 1a) is composed of 3D folded structures that has important roles for genetic transfer. However, nanometer-scale 3D folded structures of human chromosomes have not been well understood yet. It is expected that 3D-AFM contributes to chromosome study, but it is difficult to measure inside of 3D folded structures of chromosomes by conventional conical tip without damage of samples by tip scanning. To visualize 3D folded structures of chromosome by 3D-AFM, we fabricated a carbon nanotube (CNT) tip (length > 500 nm, diameter < 20 nm) to penetrate chromosomes by 3D-AFM. By using the conventional tip and home-made CNT tip (Fig. 1c(i)-d(i)), we performed 3D-AFM of human chromosomes, and obtained 3D frequency shift (Δf) image (Fig. 1b). We extracted single Δf curves from the 3D Δf images obtained with Si tip and CNT tip, respectively (Fig. 1c(ii)-d(ii)). Δf curve using CNT tip shows oscillatory profile until 500 nm in depth from the surface of the chromosome in contrast to the Δf curve using Si tip. This result suggests that the obtained 3D Δf image using CNT tip reflects structures inside chromosome. Based on this research, applications of 3D-AFM will be expanded for visualizing 3D structures of biological samples in various research fields.

3:20pm **BI+AS+HC+SS-MoA-6 Mass-Manufactured Surface Textures Kill Bacteria as Part of Low-Cost Water Purification Devices***, **Liza White**, C. Howell,* University of Maine

Water purification and disinfection, particularly of turbid water, is a significant and growing need worldwide. Pulsed electric field (PEF) devices can be used to inactivate pathogens in water; however, manufacturability, power consumption, cost, and portability remain significant hurdles. Through leveraging paper industry technology in Maine, we have optimized electric field generation using custom textured film in a roll-to-roll manufacturing process to act as the functional part of portable PEF water purification devices. Specifically, we used commercially produced textured release paper as a substrate for the film electrodes and explored different types of metal coating to reduce the overall power consumption, cost, and manufacturability. CAD and modeling software was then used to simulate various textures to determine the optimal texture to focus the electric field while keeping a low total current density, and a custom texture was designed. The mass-manufactured textured materials were cut into singular flow cells and were sputter-coated with various metals and assembled. The flow cells were connected to a pulsed generator that pulsed a square wave at 15 µs at a frequency of 100 Hz with a voltage of 100 V. Water with a known concentration of bacteria was pushed through the flow cells at a rate of 200 µL/minute. The outlet sample was collected, and bacterial reduction was calculated. These tests demonstrated that mass-manufactured surface textures could function as part of a low-cost PEF water purification device. The development of low-cost PEF water purification devices based on surface texture will help provide more accessible clean water in the face of growing water shortages.

4:00pm **BI+AS+HC+SS-MoA-8 Nature-inspired Materials for Energy and Environmental Sustainability***, **Tak Sing Wong**,* The Pennsylvania State University **INVITED**

With an evolutionary history of 3.95 billion years and over 8 million species on earth, natural organisms have often served as blueprints for the design of highly functional engineered materials. In particular, natural species have demonstrated how different micro/nanoscale surface architectures can yield an array of distinct interfacial functions. Understanding the fundamental principles behind these natural surfaces will aid the design of multifunctional materials for a range of energy and sustainability applications. In this talk, I will discuss a number of specific examples showcasing our recent biologically inspired technologies which take inspirations from insects to plants. These examples include the development of anti-fouling and self-cleaning surfaces inspired by the slippery rims of the *Nepenthes* pitcher plants, as well as the fabrication of ultra-antireflective coatings inspired by the leafhopper-produced brochosomes. Perspectives on how nature-inspired materials may impact future applications in energy and sustainability will be discussed.

4:40pm **BI+AS+HC+SS-MoA-10 Programmable Biomimetic Light-Harvesting Systems: Quantum-Optical Control of Light-Matter Interactions***, A. Lishchuk, E. Csanyi, **Graham Leggett**,* University of Sheffield, UK

The absorption of light by molecules leads to the formation of excitons (electron-hole pairs). Control of excitons is essential for many new and emerging technologies, but the inefficient dynamics and short diffusion lengths (~ 10 nm) of excitons in molecular systems limit their utilisation.Theory suggests that exciton diffusion lengths could be enhanced by several orders of magnitude in the strong light-matter coupling regime. However, design principles for the production of photonic materials that exploit strong coupling are lacking. We have found that photosynthetic light-harvesting complexes (LHCs) from plants and bacteria are strongly coupled to localised surface plasmon resonances (LSPRs) in arrays of metal nanostructures, yielding macroscopically extended excited states that enable coherent, non-local excitation transfer and the creation of bespoke optical states not found under weak coupling. However, proteins are not suitable for putative applications of molecular photonic materials. Inspired by photosynthetic LHCs, we demonstrate the fabrication of programmable plexcitonic antenna complexes, in which polymer scaffolds organise excitons within localised surface plasmon resonances to achieve strong light-matter coupling, yielding delocalised excited states (plexcitons) that extend across at least 1000s of pigments. In our plexcitonic antenna complexes, poly(amino acid methacrylate) scaffolds grown from gold nanostructures by atom-transfer radical polymerisation (ATRP) organise excitons (transitions in chlorophylls) within LSPRs to achieve strong light-matter coupling, yielding Rabi energies up to twice as large as those achieved with biological LHCs. The energies of the resulting delocalised excited states (plexcitons) are programmed by varying the degree of polymerisation, scaffold packing density and chlorophyll loading. Steric hinderance in fully-dense PCysMA brushes limits binding of bulky chlorophylls, but the chlorophyll concentration can be increased to ~2M, exceeding that in biological light-harvesting complexes, by controlling the grafting density and polymerisation time. Moreover, synthetic plexcitonic antenna complexes display pH and temperature responsiveness, facilitating active control of strong plasmon-exciton coupling. These biologically-inspired metamaterials offer great promise for the design of new types of molecular photonic device.

5:00pm **BI+AS+HC+SS-MoA-11 Microfluidic QCM with Ultrahigh Q-Factor: A New Paradigm for Acoustic Biosensing?***, Y. Zhao,* Duke University*; Z. Parlak,* Qatch LLC.*; M. Yu,* Duke University*; D. French,* Qatch LLC.*; W. Aquino, **Stefan Zauscher**,* Duke University

Acoustic thickness shear mode transducers, such as the quartz crystal microbalance (QCM), can provide high throughput biomolecular detection for diagnostics with minimal sample preparation. A QCM's resonance frequency change (Δf) is generally related to the mass change (Δm) due to analyte binding on the sensor surface. If equipped with dissipation monitoring, a QCM's dissipation (D or ΔD) is related to the viscoelastic properties of the surface-bound analyte. Although current QCM sensors are simple and robust devices, they generally require high sample volumes and suffer from low sensitivity/resolution due to fluid damping.

We show that by adding microfluidic channels onto QCM sensors, we can strongly couple small amounts of liquid within the channels to the sensor, thereby largely eliminating fluid damping. This coupling eliminates dissipation effects during shear excitation and thus dramatically increases the quality factor (Q-factor) of the sensor and allows for accurate measurement of changes in fluid density, and therefore also for biomolecular mass measurements in liquid environments.

The abrogation of damping effects arises from the almost lossless coupling of the liquid to the side walls of the channels, which results in an in-plane pressure wave. We found that if the wavelength of the pressure wave is considerably longer than the channel width, the liquid inside the channels is strongly coupled to the channel walls and thus damping is suppressed. Since viscous effects are largely eliminated, the microfluidic QCM (µ-QCM) is also insensitive to temperature-induced viscosity changes. With a high Q-factor, direct data interpretation, pure mass sensitivity and temperature insensitivity, and small device size, the µ-QCM provides a new paradigm for acoustic biosensing.

We used Finite Element Analysis (FEA) to test our hypothesis that the in-plane pressure wave generated by the channel side walls is responsible for the enhanced performance of the µ-QCM. Furthermore, we conducted a nondimensional analysis to reveal the most important parameters, including channel dimensions, crystal thickness, and fluid viscosity/density, and how they affect the dissipation. This knowledge can be easily extended to other acoustic bio-transducers to improve their sensitivity/resolution.

Finally, we show the design and microfabrication of µ-QCM devices, and their testing with a range of liquids with known viscosity and density, to demonstrate the high Q-factor of µ-QCMs and to demonstrate the latter's ability to sense density changes (unencumbered by viscosity) in small (~nL) sample volumes.

Fundamental Discoveries in Heterogeneous Catalysis Focus Topic

Room 321 - Session HC+AS+SS-MoA

Advances in Materials and Analysis in Heterogeneous Catalysis I

Moderators: Dan Killelea, Loyola University Chicago, **Swetlana Schauermann**, Christian-Albrechts-University Kiel, Germany

2:00pm **HC+AS+SS-MoA-2 Electrocatalytic Activity of Size-Selected Sub-Nano Pt Clusters Toward the Hydrogen Evolution Reaction***, **Tsugunosuke Masubuchi,*** University of Utah*; S. Kumari, Z. Zhang, P. Sautet, A. Alexandrova,* University of California at Los Angeles*; H. White, S. Anderson,* University of Utah

Platinum is known to exhibit high electrocatalytic activity toward the hydrogen evolution reaction (HER). From a sustainable point of view, sub-nano Pt clusters can be promising HER electrocatalysts because their electrochemically active surface area per mass is much larger than that of bulk Pt or larger Pt nanoparticles. There are fundamental questions, however, about the nature of the HER mechanism, including the electronic and structural properties of the catalytic sites required.

To this end, we studied the HER activity of atomically size-selected sub-nano Pt clusters deposited on conductive oxide supports. The electrodes of sub-nano Pt clusters were prepared using a home-built cluster beam deposition instrument, which consists of a laser vaporization cluster source, a mass-selecting ion beamline, and an ultrahigh vacuum (UHV) end station for cluster deposition. The oxide substrates were cleaned in advance by Ar^+ sputtering and annealing and tested to ensure that they are electrochemically inactive. Ions of size-selected sub-nano Pt clusters were deposited on the substrates until a certain coverage was reached. The sample electrodes prepared in this way were exposed to an O_2-free $HClO_4$ electrolyte solution, and electrochemical measurements were performed.

In this contribution, we will discuss how every Pt atom counts for the HER activity of size-selected sub-nano Pt clusters. We will particularly show that by the interplay between the experiment and quantum chemical calculations, certain Pt clusters, composed of only several atoms, can reduce protons and adsorb hydrogen atoms very efficiently, which leads to their superior HER activity.

2:20pm **HC+AS+SS-MoA-3 In situ X-ray Absorption Spectroscopy to Probe the Dynamics of Ni_3Fe catalysts: Implications for Dry Methane Reforming***, L. Cruz,* University of California, Riverside*; J. Hong,* Stanford Institute for Materials and Energy Sciences, SLAC National Accelerator Laboratory*; S. Shah,* University of California - Riverside*; S. Bare,* Stanford Institute for Materials and Energy Sciences, SLAC National Accelerator Laboratory*; **Kandis Leslie Gilliard-AbdulAziz,*** University of California - Riverside **INVITED**

The exsolution of nanoparticles from perovskite precursors has been explored as a route to synthesize firmly anchored catalysts. The characteristics of these exsolved nanoparticles, such as size, composition, and morphology, are highly dynamic depending on the redox nature of the reactive environment. Their dynamic nature warrants a study that tracks the changes with in-situ and ex-situ characterization to benchmark states. In this talk, we will discuss the use of operando X-ray Absorption Spectroscopy (XAS) to study the formation, evolution, and regeneration of exsolved NiFe nanoparticles from $LaFe_{0.8}Ni_{0.2}O_3$ perovskite oxide precursors. STEM-HAADF with EDS analysis was used to measure the nanoparticle composition and morphology after exposure to dry methane reforming (CH_4, CO_2, CO, H_2, H_2O), reductive (H_2) or oxidative (O_2) conditions. Our findings show that the nanoparticle formation in 5%H_2/He occurs in sequential exsolution mechanisms where Ni exsolves first and then Fe. During DRM conditions, the Ni composition transforms from predominantly Fe-rich to Ni-rich NiFe catalysts. Lastly, we will discuss the regeneration of bimetallic alloys and implications for future work in exsolved bimetallic alloys.

3:00pm **HC+AS+SS-MoA-5 Photocatalysis between High-Purity and Applied Reaction Conditions: Understanding Carbon Dioxide Reduction on the Molecular Level***, **Jennifer Strunk,*** Leibniz Institute for Catalysis, Germany **INVITED**

Reducing carbon dioxide just with the energy of (sun)light to platform chemicals for the chemical industry (e.g. carbon monoxide, methane) is still a highly desirable process to enable a recycling of this greenhouse gas. Yet, despite more than 40 years of research, the achievable yields in photocatalytic carbon dioxide reduction have not increased significantly, thereby clearly failing to meet demands for industrial implementation. One significant hurdle is our limited understanding of the chemical processes on the molecular scale, in particular under reaction conditions relevant to a future application. This is to a large extent due to the vastly different, and in part badly described, reaction conditions applied in published works, making it practically impossible to compare the different studies.

Our approach is the design of a reactor and a research methodology to enable highly reproducible studies in photocatalytic carbon dioxide reduction. Using solely construction parts suitable for high vacuum applications, we have developed the so-called "high-purity gas-phase photoreactor" with gas chromatographic trace gas analysis, allowing to obtain reproducible results on the ppm level. It can also function as bridge between true single-crystal studies and possible reaction conditions in practical applications.

Using this device, fair comparisons of different photocatalysts suggested in literature has been possible. This revealed the well-known titanium dioxide as one of the best materials, despite its large bandgap. Reliable apparent quantum yields have been determined. Focusing our studies on titania, it has been possible to obtain a rather complete picture of the reaction progress on the molecular scale. The reaction from carbon dioxide to methane is likely not a linear sequence of reduction steps but involves also oxidative steps by a reaction with holes. Even if methane as one-carbon product is formed, intermediates involving a C-C bond are involved. The limiting step is the water oxidation reaction, which does not run to completion. Instead, oxygen-related species are stored on or in titania until the material is saturated and the reaction ceases. These findings indicate that (i) completely other materials, possibly Z scheme systems with suitable cocatalysts, need to be developed that allow a less complex surface reaction pathway, and (ii) that (biogenic) methane may be a better co-reactant than water in a "photo dry reforming" reaction.

4:00pm **HC+AS+SS-MoA-8 Electrocatalytic Nitrate Reduction: Controlling Adsorbate Affinity to Tailor Reaction Products***, **Kelsey Stoerzinger,*** Oregon State University **INVITED**

The electrochemical nitrate reduction reaction (NO_3RR) represents a distributed approach for water treatment and chemical synthesis (ammonia) as an alternative to conventional carbon-intensive processes

(Haber-Bosch). Catalysts requirements for this reaction, however, are immense: water/protons are required to reduce nitrate but compete with NO_3RR to evolve hydrogen gas at comparable potentials, and selectivity along an 8 e^-/10 h^+ process is required to produce ammonium. Here we investigate NO_3RR activity and ammonium selectivity across 3d and select 4d transition metals in neutral conditions prototypical of nitrate-containing source waters, developing fundamental understanding of the competitive processes that give rise to these trends to guide future catalyst design. We develop a microkinetic model capturing the potential-dependent nitrate rate order, arising from competitive adsorption between nitrate and hydrogen. Competition with the hydrogen evolution reaction is manifest in the NO_3RR Faradaic efficiency, described by catalyst work function. Selectivity to ammonium nominally increases as transition metal d-band center energy approaches and overcomes the Fermi level, with Co representing an optimal catalyst. Density functional theory calculations identify a Sabatier-like relationship between ammonium selectivity and the driving forces for nitrite reduction to nitric oxide and the dissociation of nitric oxide, where Co represents a local optimum between these two processes. These results identify competing design considerations – linking electronic structure to mechanistic selectivity-limiting steps – offering strategies to improve existing catalysts and design new alloy compositions for NO_3RR to ammonium.

4:40pm **HC+AS+SS-MoA-10 Energetics and Growth Modes of Ni and Pd Nanoparticles on Graphene / Ni(111)*, Kun Zhao*,** *J. Rumptz, N. Janulaitis, C. Campbell,* University of Washington

The use of carbon supports for late transition metal nanoparticle catalysts has grown substantially in recent years due to efforts to develop electrocatalysts for clean energy applications and catalysts for new aqueous-phase biomass-related conversions, and due to the evolution of new carbon materials with unique properties (e.g., graphene, carbon nanotubes, etc.). However, much less is known about the bonding energetics of catalytic metal nanoparticles on carbon supports in comparison with oxide supports, which are more common for thermal catalysis. Here we investigated the growth morphologies and heats of adsorption of Ni and Pd vapor deposited onto graphene/Ni(111) at 300 K and 100 K using He^+ low-energy ion scattering (LEIS) and single crystal adsorption calorimetry (SCAC). For Ni/graphene/Ni(111), the SCAC results showed at 300 K the heat of adsorption of Ni vapor increases rapidly from 336 kJ/mol initially to the heat of sublimation (430 kJ/mol) by 2 ML, and at 100 K from 230 kJ/mol to the heat of sublimation slower by 3.5 ML. The growth models derived from LEIS results suggested that Ni grows as flat-topped islands with a thickness of ~1.5 nm when deposited at 300 K, and small hemispherical cap shape with a number density of 2×10^{16} particles/m^2 when deposited at 100 K. The particle size and morphology account for the differences in the heat of adsorption versus coverage at these two temperatures. The Ni chemical potential as a function of average particle diameter in the 0.5 to 4 nm range at 100 K was determined from the LEIS and SCAC measurements, and an adhesion energy of 3.6 J/m^2 was determined from fitting the chemical potential vs diameter to a theoretical model. For Pd/graphene/Ni(111), the heats of adsorption of Pd increase with coverage similarly to Ni at 300 K and 100 K and reach the heat of sublimation (370 kJ/mol) by 2.8 ML, with an initial heat of adsorption at 300 K (272 kJ/mol) that is 47 kJ/mol higher than at 100 K. The trends in the heat of adsorption are supported by the growth model from the LEIS results. Similar to Ni growth, however with much smaller particle size and larger particle density, Pd grows as flat-topped islands at 300 K with a thickness of ~0.85 nm, and hemispherical cap shape at 100 K with a number density of 6×10^{16} particles/m^2. The evolution of Pd chemical potential along with particle size was determined in the average particle diameter range of 0.6 – 2.5 nm at 100 K and the adhesion energy was found to be 3.8 J/m^2.

5:00pm **HC+AS+SS-MoA-11 Size Dependent CO_2 Reduction Activity and Selectivity of Ag Nanoparticle Electrocatalysts in sub-5 nm Regime*, Xingyi Deng,*** NETL/LRST*; D. Alfonso,* NETL*; T. Nguyen-Phan,* NETL/LRST*; D. Kauffman,* NETL

Coinage metals (Au, Cu and Ag) are state-of-the-art electrocatalysts for the CO_2 reduction reaction (CO_2RR). Size-dependent CO_2RR activity of Au and Cu has been studied, and increased H_2 evolution reaction (HER) activity is expected for small catalyst particles with high population of undercoordinated corner sites. A similar level of consensus is lacking for Ag catalysts because the ligands, capping agents, or stabilizers typically used to control particle size and crystallographic orientation can block specific active sites and mask inherent activity trends. We used a combination of ultrahigh vacuum surface science techniques, electrochemical measurements, density functional theory, and microkinetic modeling to finely resolve the size dependent CO_2RR activity and selectivity of Ag nanoparticle electrocatalysts in the sub-5 nm range. Experimental results identified CO_2RR selectivity increased with average particle diameter between 2 to 6 nm with 3.7 ± 0.7 nm diameter Ag particles demonstrating the highest combination of CO_2RR activity and selectivity. A nearly identical size-dependent trend was also predicted in computational modeling: smaller diameter particles favored H_2 evolution reaction (HER) due to a high population of Ag edge sites, whereas larger diameter particles favored CO_2RR as the population of Ag(100) surface sites grew. Our results resolve the CO_2RR behavior of Ag in the crucial sub-5 nm range and establish an effective minimum size limit for balancing activity and selectivity. Particles below a critical diameter suffered from poor selectivity, while larger particles above the critical diameter demonstrated bulk-like activity that led to reduced catalyst utilization. These results provide insight into the size-dependent CO_2RR activity of pristine Ag catalysts and will help guide future catalyst development efforts.

MEMS and NEMS Technical Group

Room 302 - Session MN+2D-MoA

Emerging Materials and Structures for MEMS/NEMS Devices

Moderators: Azadeh Ansari, Georgia Institute of Technology, **Yanan Wang**, University of Nebraska - Lincoln

1:40pm **MN+2D-MoA-1 Phononic Crystals based on Two-Dimensional Materials*, Yanan Wang,*** University of Nebraska - Lincoln **INVITED**

Thanks to the ultimate thinness, excellent elastic properties, and unparalleled advantages in device integration, two-dimensional (2D) materials have emerged as compelling candidates for enabling high frequency nano-/microelectromechanical systems (NEMS/MEMS). This talk will discuss the further exploration of 2D materials in phononic devices, such as quasi-1D phononic waveguides and tunable phononic crystal lattices, emphasizing their potential applications in quantum information processing and quantum sensing systems.

2:20pm **MN+2D-MoA-3 Scaling Acoustics into mm-Wave: Higher-Order Lamb Mode Devices in Piezoelectric Thin Films*, Ruochen Lu,*** *J. Kramer, S. Cho, O. Barrera,* The University of Texas at Austin **INVITED**

The evolving wireless communication moves to higher frequency bands with broader bandwidth for faster data rate. New types of front-end elements are required to perform the signal processing at the new bands. Acoustic devices are among the processing candidates, thanks to their compact footprints and low loss. However, It has been a long-standing challenge to scale piezoelectric resonators beyond 6 GHz without significantly losing quality factor (Q) and electromechanical coupling (k^2).

Until now, three approaches have been investigated, including reduced wavelength, higher-order modes, and multi-layer periodically poled piezoelectric films (P3F) structures. The first method requires small feature sizes, e.g., the electrode pitch width of laterally vibrating devices or the thickness of film bulk acoustic wave resonators (FBARs). The direct scaling inevitably leads to fabrication challenges and more importantly, severely reduced Q from the electrical resistance and acoustic damping. The second approach utilizes the additional thickness component in higher-order Lamb modes to relax the lateral feature size requirement. However, sub-400 nm piezoelectric thin films are needed if operated at the first-order thickness mode, e.g., first-order antisymmetric (A1) mode, inducing limited Q below 500 from the surface damages during the implementation. Alternatively, one can operate at higher frequencies using increased thickness mode order acoustic modes, e.g., second-order antisymmetric (A2) mode. Nevertheless, further increasing the mode order in the thickness direction without modifying the transducer configuration leads to reduced k^2, as the generated charge tends to cancel out, limiting the applications.

Recently, we proposed the P3F platforms using thin-film lithium niobate ($LiNbO_3$) to address the challenge. By stacking transferred thin-film $LiNbO_3$ with alternating orientations in the thickness direction, we can achieve remarkable frequency scaling without losing k^2 or relying on thinner films. Complementarily oriented bi-layer acoustic resonator (COBAR) following thickness-shear modes have been demonstrated. We will report COBARs leveraging the thickness-extensional (TE) modes at 15.8 GHz using sixth-order antisymmetric (A6) mode COBAR with a high loaded Q of 720. The measured loaded Q and $f{\cdot}Q$ product ($1.14{\times}10^{13}$) are among the highest for piezoelectric acoustic resonators beyond 6 GHz.

3:00pm **MN+2D-MoA-5 AlScN Piezoelectric Metamaterials for Next Generation RF Systems***, C. Cassella, **Dan Zhao**,* Northeastern University **INVITED**

In the last two decades, microacoustic resonators (µARs) have played a key role in integrated 1G-to-4G radios, providing the technological means to achieve compact radio frequency (RF) filters with low loss and moderate fractional bandwidths (BW<4%). More specifically, Aluminum Nitride (AlN) based filters have populated the front-end of most commercial mobile transceivers due to the good dielectric, piezoelectric and thermal properties exhibited by AlN thin-films and because their fabrication process is compatible with the one used for any Complementary Metal Oxide Semiconductor (CMOS) integrated circuits (ICs). Nevertheless, the rapid growth of 5G and the abrupt technologicalleap expected with the development of sixth-generation (6G) communication systems are expected to severely complicate the design of future radio front-ends by demanding Super-High-Frequency (SHF) filtering components with much larger fractional bandwidths than achievable today. Even more, the recent invention of on-chip nonreciprocal components, like the circulators and isolators recently built in slightly different CMOS technologies, has provided concrete means to double the spectral efficiency of current radios by enabling the adoption of full-duplex communication schemes. Nevertheless, for such schemes to be really usable in both military and commercial wireless systems, self-interference cancellation networks including wideband, low-loss and large group delay lines are needed. Yet, the current on-chip delay lines that are also manufacturable through CMOS processes, which rely on the piezoelectric excitation of Surface Acoustic Waves (SAWs) or Lamb Waves in piezoelectric thin films, have their bandwidth and insertion-loss severely limited by the relatively low electromechanical coupling coefficient exhibited by their input and output transducers. As a results, these components are hardly usable to form the delay lines forming any desired self-interference cancelation networks. In order to overcome these challenges, only recently, new classes of microacoustic resonators and delay lines exploiting the high piezoelectric coefficient of Aluminum Scandium Nitride (AlScN) thin films and the exotic dispersive features of acoustic metamaterials have been emerging. These devices rely on forests of locally resonant piezoelectric rods to generate unique modal distributions, as well as unconventional wave propagation features that cannot be found in conventional SAW and Lamb wave counterparts. In this talk, the design, fabrication and performance of the first microacoustic metamaterials based resonators and delay lines will be showcased.

4:00pm **MN+2D-MoA-8 Fabrication, Actuation and Control of 3D-Printed Microscale Robots***, **Azadeh Ansari**,* The Georgia Institute of Technology **INVITED**

This talk covers the fabrication methods of micro scale robots using two photon lithography nanoscale 3D printing of various micro robot designs for biomedical applications. The polymer-based 3D printed robots are integrated with piezoelectric actuators, or magnetic thin films/cubes. Tiny polymer legs/bristles and contacts are designed for precise robot motion control. Furthermore, the microbots are equipped with various mechanical add-ons such as micro-tips/needles for penetration into soft tissues, micromanipulators, micro-drillers, and PH sensitive drug delivery units.

4:40pm **MN+2D-MoA-10 Fabrication of Resistor-based Zinc Devices using Selective Chemical Deoxidation of Screen Printed Zinc Inks by Inkjet Printing***, A. Radwan*[1]**,** Case Western Reserve University*; Y. Sui,* University of Colorado at Boulder*; **Christian Zorman**,* Case Western Reserve University

Zinc (Zn) is a common metal that harmlessly decomposes in the environment and thus is considered a leading metal for use in environmentally-friendly electronics. Zn readily oxidizes under ambient conditions forming a thin, electrically-insulating zinc-oxide (ZnO) layer on the surface of Zn particles. Fortunately, conductive Zn structures can be formed by etching the ZnO layer using aqueous solutions of acetic acid dispensed by drop casting. Although drop-casting is simple to implement, dispensing extremely small volumes is difficult . As such, drop casting is limited to producing structures with high conductivity (i.e., electrodes) but is not suitable to produce structures with tunable resistivity.Although designed to dispense inks, inkjet printers are precision liquid dispensing systems capable of depositing picoliter droplets at designated locations. Therefore, it is feasible to use an inkjet printer as an acetic acidic dispenser to form Zn structures by selective etching of Zn-based inks. Unlike drop casting, this reactive inkjet printing (RIJ) process enables the resistivity of Zn structures to be tuned by controlling the amount of acetic acid dispensed. Moreover, inkjet printing offers precision lateral control of the dispensing process which could enable the fabrication of both conductive and resistive structures in the same Zn layer.

In this paper, a selective RIJ method to dispense an etching agent on screen printed Zn structures with a high degree of volumetric and spatial control is described. This RIJ process is used in conjunction with screen printing to precisely control the amount of acetic acid deposited on the surface of printed Zn structures. The number of print passes and drop spacing are utilized to precisely regulate the exposure of the Zn structures to acetic acid thus enabling unparalleled control of the etching process. The screen printing and RIJ processes are performed at room temperature, making them compatible with temperature sensitive substrates including many that are attractive for flexible, implantable and biodegradable electronics. The substrate only needs to be inert to acetic acid. This study specifically focuses on the formation of Zn structures with tunable resistivity and explores the relationships between key printing parameters and electrical resistivity of the resulting Zn structures. As process demonstrators, microheaters and RC filters are fabricated and characterized.

5:00pm **MN+2D-MoA-11 Mechanically Tunable One-Dimensional Photonic Crystals Fabricated by Two-Photon Polymerization***, **Victoria P. Stinson**[2], N. Shuchi, M. McLamb, G. Boreman, T. Hofmann,* University of North Carolina at Charlotte

Photonic crystals have attracted interest in optical applications, due to their highly reflective photonic bandgaps [1-3]. These photonic bandgaps are formed by creating a dielectric periodicity. Depending on the complexity of this periodicity the photonic crystal can be described as being one-, two-, or three-dimensional. In the one-dimensional case, this periodicity is created in a single direction. One-dimensional photonic crystals fabricated by two photon polymerization have demonstrated high-contrast photonic bandgaps in the infrared spectral range [2]. This is achieved by alternating layers of high- and low-density. In order to allow additional spectral filtering of the photonic bandgap, defects have also been implemented into these designs, allowing narrow band transmissions to exist within the otherwise reflective photonic bandgap [3]. While the spectral position of these features can be easily designed for a desired range, there are currently few methods for manipulating these features post-fabrication. Introducing mechanically sensitive flexures as low-density layers into these one-dimensional photonic crystals could fill this gap. Opto-mechanical devices fabricated by two-photon polymerization is an emerging field which has applications in areas such as MEMS and microrobotics [4]. The ability to control the spectral response via an external mechanical stimuli opens the door for more complex and adaptable sensing and filtering bandgap devices. The use of two-photon polymerization in the development of these devices allows for three-dimensional design freedom with efficient fabrication times. In this study we report on the use of sub-wavelength mechanical flexures in the low-density layers of one-dimensional photonic crystals fabricated by two-photon polymerization. Upon compression the change in thickness of these low-density layers will result in an overall spectral shift of the photonic bandgap. The degree of spectral shifting, as well as an analysis of the mechanical properties of one-dimensional photonic crystals with flexures are presented and discussed.

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[2] Y. Li, D. Fullager, S. Park, D. Childers, R. Fesperman, G. Boreman, T. Hofmann, Opt. Lett. **43**, 4711-4714 (2018).

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[4] Z. Lao, N. Xia, S. Wang, T. Xu, L. Zhang, Micromachines **12**, 465 (2021).

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[1] **MEMS/NEMS Best Research Work Award**

[2] **MEMS/NEMS Best Research Work Award**

Manufacturing Science and Technology Group
Room 305 - Session MS+AP+AS+TF-MoA

Advanced Characterization and Metrology for 3D and ML for Microelectronics Materials Discovery

Moderators: Alain Diebold, SUNY Polytechnic Institute, **Jeremy Mehta**, U.S. Department of Energy

1:40pm **MS+AP+AS+TF-MoA-1 Semiconductor Metrology for Dimensional and Materials Scaling*, Bryan Barnes,*** NIST **INVITED**

Dimensional and materials scaling are two key drivers for advancing computational capabilities beyond the conventional scaling trends of the last several decades. Future device metrology solutions must be developed now without clarity as to which combinations of proposed architecture(s) and novel materials will prove best suited for integration into high-volume manufacturing. This presentation briefly reviews these possible pairings and the near-term and long-term metrology challenges as identified in the *IEEE International Roadmap for Devices and Systems*. As device dimensions further approach near-atomic and atomic scales, many of the several existing metrology techniques will face new tests, illustrated here using examples and solutions from our optics-based semiconductor metrology research. No single metrology technique can address all issues faced in modern process control and inspection; thus we address complementary techniques across semiconductor metrology are required to address dimensional and materials scaling

2:20pm **MS+AP+AS+TF-MoA-3 Towards a Digital Twin for Spatiotemporal Experiments*, Subramanian Sankaranarayanan,*** Argonne National Laboratory **INVITED**

We will present our ongoing efforts at creating a virtual platform or "DigitalTwin", wherein the users can exhaustively explore experimental controls and obtain synthetic read-outs – a small subset that displays the most interesting physics and/or phenomena can be explored in the actual experiments. We take advantage of the fact that most experimentalspatiotemporally-resolved measurements at SUFs in real or reciprocal space can be derived from the accurate prediction of atomic configurations and their dynamical evolution across time- and length. We will use representative examples to demonstrate how Digital Twins can be utilized for accelerated materials discovery and design.

3:00pm **MS+AP+AS+TF-MoA-5 Autonomous Scanning Probe Microscopy: from Streaming Image Analysis to Learning Physics***, S. Kalinin,* ***Yongtao Liu,*** Oak Ridge National Laboratory **INVITED**

Machine learning and artificial intelligence (ML/AI) are rapidly becoming an indispensable part of physics research, with domain applications ranging from theory and materials prediction to high-throughput data analysis. However, the constantly emerging question is how to match the correlative nature of classical ML with hypothesis-driven causal nature of physical sciences. In parallel, the recent successes in applying ML/AI methods for autonomous systems from robotics through self-driving cars to organic and inorganic synthesis are generating enthusiasm for the potential of these techniques to enable automated and autonomous experiment (AE) in imaging.

In this presentation, I will discuss recent progress in automated experiment in scanning probe microscopy, ranging from real-time image segmentation to physics discovery via active learning. The applications of classical deep learning methods in streaming image analysis are strongly affected by the out of distribution drift effects, and the approaches to minimize though are discussed. I will further illustrate transition from post-experiment data analysis to active learning process, including learning structure-property relationships and materials discovery in composition spread libraries. Here, the strategies based on simple Gaussian Processes often tend to produce sub-optimal results due to the lack of prior knowledge and very simplified (via learned kernel function) representation of spatial complexity of the system. Comparatively, deep kernel learning (DKL) and structured Gaussian Processes methods allow to realize both the exploration of complex systems towards the discovery of structure-property relationship, and enable automated experiment targeting physics (rather than simple spatial feature) discovery. The latter is illustrated via experimental discovery of ferroelectric domain dynamics in piezoresponse force microscopy. For probing physical mechanisms of tip-induced modifications, I will demonstrate the combination of the structured Gaussian process and reinforcement learning, the approach we refer to as hypothesis learning. Here, this approach is used to learn the domain growth laws on a fully autonomous microscope. The future potential of Bayesian active learning for autonomous microscopes is discussed.

4:00pm **MS+AP+AS+TF-MoA-8 New in-Line Metrology for Advanced Semiconductor Nodes*, Cornel Bozdog,*** Onto Innovation **INVITED**

Scaling in Semiconductor Device Manufacturing means "more devices per unit area". The traditional "device shrink" scaling path was already replaced by "stack vertically" in non-volatile memory devices, now up to few hundred devices occupying the same real estate on the wafer, and growing. Gate all-around allowed logic devices to stack multiple transistors, and volatile memory is following suit. Different devices and sub-devices are now bonded together to further optimize scaling. To integrate, optimize and control the multi-thousand-step manufacturing line, in-line metrology plays the critical role. Here we will review the metrology challenges for Advanced 3D devices, present the latest advancements in traditional optical, scatterometry, electron-beam and atomic force techniques, and discuss novel x-ray, acoustic, and mid-IR metrology solutions that enable accurate profile reconstruction, in-device characterization and hybrid metrology schemes.

4:40pm **MS+AP+AS+TF-MoA-10 Applications of Artificial Intelligence AI and Machine Learning ML to Semiconductor Materials Discovery and Optimization*, Brian Valentine,*** DOE **INVITED**

Semiconductor elements such as silicon and gallium are applied in a wide variety of electronic, optical, and energy conversion applications; new elemental, compound, and dopant compositions are continually sought to improve known semiconductor characteristics to find unknown but desired semiconductor material characteristics. In this paper some applications of AI and ML to semiconductor material design and optimization are reviewed, along with limitations of AI and ML techniques applied to materials design and development and forward directions in these materials design and development methods.

Nanoscale Science and Technology Division
Room 304 - Session NS1+AS+EM-MoA

Correlative Microscopy for Nanoscale Characterization

Moderators: Sidney Cohen, Weizmann Institute of Science, Israel, **Georg Fantner**, EPFL, Switzerland

1:40pm **NS1+AS+EM-MoA-1 Large Volume 3D Biological Imaging with Electron and Cryo-Super-Resolution Microscopy*, Harald Hess,*** HHMI, Janelia **INVITED**

Volume or 3D electron microscopy continues to expand its potential for imaging ever larger biological entities while preserving a best compromise step edge isotropic resolution of 5-10 nm. This was driven by the challenge of imaging the entire fly brain in sufficient detail for extracting the circuitry of connectome. While the resolution is not of the standards of TEM's, such resolution is of unique value when it encompasses whole cells and complete tissues.We will review the capabilities of FIB-SEM, with ~100 micron sized volumes. Numerous examples can be browsed on openorganelle.com . A cryogenic protocol involving sample vitrification, cryogenic imaging by structured illumination or by photoactivated localization microscopy then followed by staining and resin embedding can then produce the sample suitable for further FIBSEM imaging. This effectively adds protein location information as a color to the 3D EM image. Likewise, several examples correlating specific proteins in the nucleus, on membranes, on and defining organelles and vesicles. Prospects of future challenges are discussed. We will also describe a system capable of imaging volumes approaching 1 mm^3 It is based on Ion Beam Etching and Milling with a Multi beam Scanning Electron MicroscopeIBEaM MSEM.

2:20pm **NS1+AS+EM-MoA-3 The Role of SnO_2 Processing on Ionic Migration in Multi-Halide Perovskites*, Holland Hysmith,*** University of Tennessee Knoxville*; S. Park,* National Renewable Energy Laboratory*; A. Ievlev, Y. Liu,* Oak Ridge National Laboratory*; K. Zhu,* National Renewable Energy Laboratory*; M. Ahmadi,* University of Tennessee Knoxville*; J. Berry,* National Renewable Energy Laboratory*; O. Ovchinnikova,* Oak Ridge National Laboratory

Moving towards a future of efficient, accessible, and less carbon reliant energy devices has been at the forefront of energy research innovations for the past 30 years. Multi-halide perovskite (MHP) thin films have gained significant attention due to their flexibility of device applications and tunable capabilities for improving power conversion efficiency.[1] Many behavioral aspects to MHP's are thoroughly investigated: functionality of grain boundaries, recombination effects, ionic migration patterns, and hysteresis.[2-4]

Chemical Vapor Deposition (CVD) is a widely used technique for thin film coatings due to its ability for producing high volume batches of MHP's with larger grain sizes, fewer defects, and fewer grain boundary formations.[5-6] Additionally, nanoparticle processing has been applied to induce enlargement of grain boundaries, showcasing larger current signals than its MHP counterparts.[7] Therefore, how does common substrate processing techniques (i.e. CVD, nanoparticles, hybrid) influence the behavior of MHP phenomenon such as ion migration and grain boundary formation? Speculated as inducing ionic recombination and driving I-V hysteresis in MHP's, understanding how chemistry can be tuned to reduce such effects would be optimal.[8-9]

We demonstrate how a hybrid approach of CVD and nanoparticle SnO_2 substrate processing significantly improves the performance of $(FAPbI_3)_{0.97}(MAPbBr_3)_{0.03}$ perovskites in comparison to each technique utilized on its own. As shown in **Figure 1**, higher performing hybrid devices exhibit fused grain boundary formations, not seen in exclusive CVD or nanoparticle devices. Conductive Atomic Force Microscopy (c-AFM) was used to track fused boundary locations and differentiate them from topographic features. Such fusing behavior has been previously observed to showcase higher counts of current and reduce defects such has halide vacancies.[7]

In summary, to understand the chemistry behavior with respect to each device interface, Time of Flight Secondary Ionization Mass Spectrometry (ToF-SIMS) depth profiling was applied. Demonstrated in **Figure 2**, migration of K^+, Na^+, Ca^+, FA^+, MA^+ was found in hybrid devices, in addition to Ca^+ and Na^+ clustering on the perovskite/air layer. Salt clustering could be correlated to the fusing effect demonstrated in the surface morphology imaged in c-AFM. Presence of K^+ has shown to reduce defects driven by alkali iodides like NaI^- and Ca^+ can help with enlarging the bandgap layer in studies where Ca+ was used to replace Pb^+.[10-11] Furthermore, reduced separation between positive ion such as MA^+ and FA^+ from negative ions can decrease the potential responsible for I-V hysteresis.[12]

2:40pm **NS1+AS+EM-MoA-4 Nanoplastic Arrays – from Chaotic Measurements to New Order***, A. Madison, D. Westly, R. Ilic, C. Copeland, A. Pintar, C. Camp, J. Liddle,* ***Samuel M. Stavis,*** National Institute of Standards and Technology (NIST)

Nanoplastic particles are ubiquitous contaminants of the environment, and their unknown hazards are of deepening concern. Optical microspectroscopy is essential to elucidate the structure–property relationships of nanoplastic particles. However, a lack of standards that are fit for purpose limits the reliability of such measurements, resulting in a growing spate of chaotic reports. In particular, the default standard of a colloidal suspension has disadvantages, with sample preparation typically resulting in disordered arrays of nanoparticles with uncontrolled sizes on imaging substrates. Moreover, existing nanoplastic standards can have broad and asymmetric distributions of optical properties. This issue confounds inference of dimensional properties and requires further study.

Optical microspectroscopy often involves contrast from Rayleigh scattering, fluorescence emission, and Raman scattering to detect, quantify, and identify nanoplastic particles. Numerous issues limit accuracy, including optical responses that vary with nanoparticle dimensions and imaging systems that present aberration effects. These issues require standards that provide reference values of dimensional, optical, and positional properties. The latter issue is unexplored, motivating a new order of microscopy standards.

We introduce the concept of the nanoplastic array, addressing these issues. This prototype standard enables calibration, correction, and correlation of image data from multiple instruments, improving the accuracy of microspectroscopy measurements. To prove the concept, we fabricate nanoplastic arrays in nanoscale films of phenolic resin by electron-beam lithography, including both fluorescent dopants and sorbents to study optical properties that are indicators of chemical sorption and resulting hazards.

Our nanoplastic arrays feature three types of nanostructures. The simplest is a uniform film, enabling correction of non-uniform irradiance for the accurate analysis of fluorescence intensity, and providing reference spectra for Raman measurements. Building in complexity, arrays of uniform pillars provide reference dimensions and positions to correlate and calibrate multiple imaging modes. Finally, and most complex, variable pillar arrays facilitate measurements of optical properties as a function of dimensional properties, with fine gradations of pillar diameter enabling quantification of the limits of detection.

Nanoplastic arrays will enable new accuracy and reliability in optical microspectroscopy, advancing the quantitative study of nanoplastic contaminants to transform unknown hazards into known quantities.

3:00pm **NS1+AS+EM-MoA-5 Development of Nanoendoscopy-AFM for Visualizing Intracellular Nanostructures of Living Cells***,* ***Keisuke Miyazawa,*** Kanazawa University, Japan*; M. Penedo,* EPFL, Switzerland*; N. Okano, H. Furusho, T. Ichikawa, M. Shahidul Alam, K. Miyata,* Kanazawa University, Japan*; C. Nakamura,* AIST, Japan*; T. Fukuma,* Kanazawa University, Japan

Atomic force microscopy (AFM) is the only technique that allows label-free imaging of nanoscale biomolecular dynamics, playing a crucial role in solving biological questions that cannot be addressed by other major bioimaging tools (fluorescence or electron microscopy). However, such imaging is possible only for systems either extracted from cells or reconstructed on solid substrates. Thus, nanodynamics inside living cells largely remain inaccessible with the current nanoimaging techniques. Here, we overcome this limitation by the nanoendoscopy-AFM, where we fabricate a needle-like nanoprobe (diameter < 200 nm, length > 500 nm) made of Sillicon or Carbon, and insert it into a living cell directly in order to measure a force curve, and visualize 2D or 3D internal structures of living cells by the measured 3D force applied to the tip during three-dimensional tip scanning. By using this method, we measured the 3D force image of a human cancer cell (HeLa). The result clearly shows the nucleus in the living cell. In addition, our results using the developed nanoendoscopy-AFM showed undetectable changes by the previous methods such as actin fiber three-dimensional (3D) maps, and 2D nanodynamics of the membrane inner scaffold in the living cells. Unlike previous AFM methods, the nanoprobe directly accesses the target intracellular components, exploiting all the AFM capabilities, such as high-resolution imaging, nanomechanical mapping, and molecular recognition. These features of the nanoendoscopy-AFM should greatly expand the range of intracellular structures observable in living cells, and contribute to the various life science research fields.

Nanoscale Science and Technology Division
Room 304 - Session NS2+AP+BI-MoA

Fabrication and Operation of Nano-Systems

Moderator: David Czaplewski, Argonne National Laboratory

4:00pm **NS2+AP+BI-MoA-8 Control of Color Centers in Diamond using Photonic and Phononic Crystals***,* ***Kazuhiro Kuruma,*** Harvard University **INVITED**

Color centers in diamond are one of the promising solid-state quantum emitters for the realization of on-chip quantum network. In particular, SiV centers have been investigated owing to their optically accessible spins as well as large and stable zero phonon line emission in photonic nanostructures. The integration of the SiV centers into the nanostructures such as photonic crystal nanocavities has been demonstrated as an efficient spin-photon interface for various quantum applications [1]. However, SiV centers need operations at mK temperatures [2] or under static strain [3] to achieve a long spin coherence time. I will show another potential approach using phononic crystals as a way to enable the realization of a long spin coherence time at higher temperatures[4]. Our efforts aimed at efficient control of the SiV spins using diamond optomechanical cavities will also be discussed [5]. Finally, I will present our works on the integration of tin-vacancy (SnV) centers, alternatives to SiV centers for operations at higher temperatures, into free-standing photonic crystal nanocavities [6].

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4:40pm **NS2+AP+BI-MoA-10 Scalable Preparation of Intrinsically Chiral Metal Surfaces for Enantioselective Processes***, **Nisha Shukla**, A. Gellman,* Carnegie Mellon University, USA

Chiral surfaces are critical components of enantioselective heterogeneous processes such as those used to prepare enantiomerically pure pharmaceuticals. While the majority of chiral surfaces in practical use are based on achiral materials whose surfaces have been modified with enantiomerically pure chiral adsorbates, there are many inorganic materials with valuable surface properties that could be rendered enantiospecific, if their surfaces were intrinsically chiral.

This work discusses recent developments in the fabrication of intrinsically chiral surfaces exhibiting enantiospecific adsorption, surface chemistry and electron emission. We propose possible paths to the scalable fabrication of high-surface-area, enantiomerically pure surfaces and discuss opportunities for future progress.

5:00pm **NS2+AP+BI-MoA-11 Wrinkle-Induced, Scale-Dependent Mechanical Properties in Nanometer Thick Films***, **Jian Zhou**, N. Moldovan, L. Stan, J. Wen, D. Jin,* Argonne National Lab*; D. Lopez,* Pennsylvania State University*; D. Czaplewski,* Argonne National Lab

Micro- and nano-electromechanical (MEMS/NEMS) devices have relied heavily on materials typically used in electronic devices. The majority of MEMS/NEMS devices are fabricated with a top-down approach to take advantage of the corresponding highly reproducible fabrication processes associated with silicon related materials. As a natural extension, as devices move into the nanoscale regime, new materials are introduced using the same fabrication paradigms used for electronics: ultra-flat surfaces, controlled stresses, simply defined materials properties, with precision 2-dimensional or 2+ dimensional definition using lithographic techniques. New materials, such as 2D materials, began to be incorporated with great promise. However, creating 2D material films that behave like traditional silicon-related films has become challenging due to their unconventional growth/deposition techniques. A typical method for depositing a 2D film is through a transfer process, which struggles to create flat, low stress, thin films. This has led to films that have variations in properties, as observed in large deviations in values reported for parameters such as Young's modulus.

In this work, we explore the variation in properties of films as they become more 2+dimensional textured versus being ultra-flat. We measure the response of resonators fabricated from both ultra-flat and wrinkled films. The ultra-flat films follow expected behaviors with small deviations in resonant frequency and bending rigidity. However, the wrinkled films have a frequency response that is highly variable, up to 45 times that found in flat films. Additionally, we find that the increased rigidity and distribution of values is scale-dependent. As we vary the in-plane dimensions of the resonant structures, we find that the characteristic values scale with the structure dimension. This matches very well with a theoretical model proposed to describe thermal fluctuations in thin films. This opens a new paradigm for device design that allows a single film to have multiple elastic properties based solely on the patterning size. Going forward, we see this being an interesting tool in the design of devices made from single nanometer-thick films.

Plasma Science and Technology Division
Room 315 - Session PS+AS-MoA

Plasma Chemistry and Catalysis

Moderators: Michael Gordon, University of California at Santa Barbara, **Floran Peeters**, LeydenJar Technologies, Netherlands

1:40pm **PS+AS-MoA-1 Study of Plasma-Catalyst Surface Interactions for Nitrogen Oxidation***, **Michael Hinshelwood**, Y. Li, G. Oehrlein,* University of Maryland College Park

Cold atmospheric pressure plasma is a promising tool for enhancing thermal catalysis for nitrogen fixation through NO_x formation. Reactive species generated in the plasma are thought to stimulate reactions at the catalyst surface, but the specific interactions are not well understood. We use a plasma-catalysis setup that enables study of such interactions by infrared spectroscopic methods [1]. In this work the formed species of N_2-O_2 interactions in plasma and over a Pt-Al_2O_3 catalyst are analyzed. An N_2/Ar gas stream is flown through an atmospheric pressure plasma jet (APPJ) to the heated catalyst in a confined chamber, and unexcited N_2 or O_2 gas can also be admitted downstream from the plasma source to the catalyst surface. Catalyst surface species are analyzed using Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS), while gas phase species exiting the catalyst bed are analyzed with Fourier Transform Infrared Spectroscopy (FTIR). Plasma power, catalyst temperature and Ar/N_2 flow are varied to investigate plasma-catalyst interactions. Bare Al_2O_3 is additionally analyzed as a reference material to isolate the effects of the catalyst from the support. Results reveal multiple interactions on the catalyst surface. Downstream gas FTIR shows a slight increase (40%) of total N_xO_y species upon heating the catalyst from 25 ^{o}Cto 350 ^{o}C suggesting an increase in reactive nitrogen or oxygen species. Additionally, N_2Odecreases upon heating while NO_x densities rise. The catalyst also promotes oxidation of NO to NO_2 compared to the support-only case at 350 ^{o}C, a known feature of platinum catalysts.DRIFTS data reveals that the Al_2O_3 support acts to store NO_x species below 450 ^{o}C through the formation of surface nitrites and nitrates, necessitating the use of long exposure times. Correlations of downstream FTIR and DRIFTS data will be presented to untangle various interactions and isolate the processes resulting in plasma catalysis. We thank B. Bayer, Dr. A. Bhan and Dr. P. J. Bruggeman for helpful discussions. This material is based upon work supported by the U.S. Department of Energy, Office of Science, Office of Fusion Energy Sciences under award number DE-SC0020232.

2:00pm **PS+AS-MoA-2 Investigation of the Interaction Between Non-Thermal Plasma Activated Nitrogen and Metal Surfaces***, **Garam Lee**, C. Yan, W. Schneider, D. Go, C. O'Brien,* University of Notre Dame

Non-thermal plasma (NTP)-assisted catalysis has recently gained substantial interest in the heterogeneous catalysis field for enhancing catalytic activity and/or selectivity, as well as for enabling chemical transformations that neither plasma nor catalysis could deliver individually. Despite the promise, the influence of NTP activation of molecules on reactivity at a catalytic surface remains primitive. Here, we report observations of the products and reactivity of plasma-activated nitrogen (N_2) species exposed to polycrystalline Ni, Pd, Cu, Ag, and Au surfaces using a newly-designed multi-modal spectroscopic tool that combines polarization-modulation infrared reflection-absorption spectroscopy (PM-IRAS), mass spectrometry (MS), and optical emission spectroscopy (OES), combined with density functional theory (DFT) models to rationalize those observations. Observations and models indicate that NTP activation provides access to metastable surface nitrogen species that are inaccessible thermally. Those metastable species are characterized using *ex situ* X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), temperature-programmed desorption (TPD), and temperature-programmed reaction (TPR) with hydrogen (H_2) to produce ammonia (NH_3). Models and observations highlight dependence of this reactivity on the identity of the metal surface. Taken together, results shed light on the role of NTP activation on promotion of surface reactivity.

2:20pm **PS+AS-MoA-3 Long-Term Degradation of PTFE in a Low Temperature Oxygen Plasma***, **Tobias Wagner**, T. Zeller, M. Rohnke, J. Janek,* Institute of Physical Chemistry, Justus Liebig University Giessen, Germany

Atomic oxygen (AO) is the most common gas species in the Low-Earth-Orbit (LEO) and responsible for material degradation of the outer shell of satellites and spacecrafts within this space region. As the LEO is also essential for commercial space flights, the degradation process of materials exposed to AO needs to be better understood in order to prevent possibly devastating material failure. Due to its properties, low temperature oxygen plasmas are suited for material degradation studies taking place on earth instead of quite expensive space studies. Here we focus on the long-term degradation of Polytetrafluoroethylene (PTFE), which is often employed on the outside of spacecrafts and therefore exposed to AO. Up to date, there is no complete understanding of the degradation process on the molecular level, which is necessary for materials improvement and new materials development.

For the degradation studies, a self-constructed capacitively driven 13.56 MHz RF reactor was used to generate an oxygen plasma for the simulation of LEO conditions. PTFE was characterised in the pristine state and after AO treatment at different times by ToF-SIMS, XPS, SEM and confocal microscopy. During plasma treatment, the samples show a linear mass loss behaviour. ToF-SIMS surface analysis reveal mass fragments like COF^- or C_3O^+, which shows a clear chemical reaction of oxygen species with PTFE. The presence of these molecular indicators was verified by XPS, where additional carbon and oxygen species were found after treatment. SEM micrographs showed an inhomogeneous degradation on the surface in the first hours similar to actual LEO exposure. For a complete understanding of the degradation progress, mass spectrometric studies of the plasma composition are carried out in situ. Overall, the results show that the reaction of PTFE with AO is occurring on a chemical rather than a physical path, with the fragmentation of long carbon chains into smaller fragments likely driving the material degradation.

2:40pm **PS+AS-MoA-4 Study of Elastomer Degradation in Processing and Cleaning Plasma Chemistries***, **Nicholas Connolly**, D. Barlaz, R. Garza, D. Ruzic, M. Sankaran,* University of Illinois Urbana-Champaign*; N. Kolliopoulos, G. Lunardi,* DuPont Precision Parts & Solutions

Fluoroelastomer (FKM) and perfluoroelastomer (FFKM) materials are used extensively in seals for plasma processing equipment used to manufacture semiconductors. Chamber etching and cleaning processes, particularly those using fluorine chemistry, oxygen chemistry, or a mixture of both, lead to the degradation of the elastomer seals. While most decomposition products are volatile, the recognition of seals as a source of chamber contamination in the form of undesired etch products and particle generation is important for robust semiconductor manufacturing processes. Recent emphasis on coatings and filler materials for elastomer seals makes understanding of decomposition conditions an ongoing effort.

This work investigates the relationship between plasma parameters, including electron temperature, plasma density, and radical densities, and elastomer seal degradation in mixtures of $SF_6/O_2/Ar$ plasmas. Various commercial FKM/FFKM materials will be investigated. Langmuir probe analysis is used to characterize electron temperature and density (predicted T_e of 3 eV and density of 1×10^{17} m^{-3}), while in-situ thermocouple-based radical probes are used to measure radical densities of oxygen. Efforts towards the development and implementation of an in-situ fluorine radical probe will also be reported. Characterization of the elastomer surface after plasma exposure will be completed using electron microscopy and optical profilometry, as well as testing of mechanical properties of the seals.

3:00pm **PS+AS-MoA-5 Utilizing Optical Spectroscopy to Explore Mechanisms of Plasma-Assisted Catalysis in Model Exhaust Systems***, **Joshua Blechle,*** Wilkes University

With increasing concerns over the environmental presence of nitrogen oxides, there is growing interest in utilizing plasma-mediated conversion techniques. Nonthermal plasma-assisted catalysis (PAC) in particular has shown great potential for continued improvements in exhaust abatement. Advances, however, have been limited due to a lack of knowledge in regards to the fundamental chemistry of these plasma systems, and the complexity of the plasma-surface interface. The sheer number of potential catalysts and the variability in exhaust gas composition further exacerbate these issues.

In order to investigate these interactions, a number of inductively-coupled plasma systems were generated from model exhaust precursors (notably, N_2 and O_2 mixtures). Internal energies of notable diatomic species are determined via optical emission spectroscopy (OES) to explore the trends in energy partitioning with respect to plasma conditions. Repeated measurements in the presence of precious metal (Ag, Pt, and Pd) and alumina surfaces demonstrate a strong vibrational temperature (T_V) dependence with respect to applied power (25-200 W) but a somewhat limited dependence on substrate identity. In addition, very little change in N_2* and N* densities are observed, whereas there are significant decreases in both NO* and O* densities in the presence of all substrates. A series of composite ($Ag/\gamma\text{-}Al_2O_3$) catalysts with varying Ag loading are also studied, with T_V's ranging from ~2500-5100 K, with the highest temperatures reached for raw alumina systems, demonstrating a Ag-mediated vibrational quenching.

To further explore catalytic behavior, kinetic trends are observed via time-resolved OES, with rate constants determined for both the formation and destruction of relevant excited states. Correlating these data with measured densities and temperatures allows for unique insight into the plasma-surface interface and the mechanisms by which these processes occur. Expanding upon the library of system conditions and increasing the complexity of the exhaust gas model will serve as a foundation for improved design and implementation of PAC methods.

3:20pm **PS+AS-MoA-6 Gasification of Carbon and CO_2 Into CO at Low Vacuum Through Combined Plasma and Heating Exposure***, **Edwin Devid,*** DIFFER, Netherlands*; R. Van de Sanden,* DIFFER & EIRES, Netherlands*; M. Gleeson,* DIFFER, Netherlands

Atmospheric CO_2 concentrations still continue to rise in 2020 [1] and are threatening the goals of the Paris Agreement [2]. By activating CO_2 through plasma, CO_2 is reduced into CO where CO is not only a high-value chemical for the chemical industry but also allow to store renewable electricity into chemical energy via an intermittent way at the cost of CO_2 consumption. Currently, mere CO_2 dissociation through non-thermal inductively coupled Radio Frequency (RF) plasma is not economically viable to obtainboth high CO_2 conversion and energy recovery efficiencies [3,4].

In this experiment, CO_2 dissociation by plasma is assisted by the co-reactant carbon. Through this co-reactant, additional processes will take place that aids the CO_2 dissociation into CO. In low vacuum (~1.3 mbar CO_2), carbon is heated (till 1000 K, in a quartz tray) while being exposed to CO_2 plasma. This process gives increased yields of CO where O_2 gas is consumed by the dominating process: $2C + O_2 \rightarrow 2\,CO$. No evidence of the gas phase back reaction $CO + 1/2O_2 \rightarrow CO_2$ is observed. By usage of isotopic carbon^{13} and modeling of the mass spectrometric data, the different processes operating (i.e. $2C + O_2 \rightarrow 2\,CO$ versus $CO_2 \rightarrow CO + 1/2O_2$ and $CO_2 + C \rightarrow 2\,CO$) are disentangled. Under a buildup ~1.3 mbar CO_2 atmosphere plus combined plasma and heat exposure upon the carbon gives, with increasing temperature a steeply rising of emitted CO at the cost of declining O_2 and CO_2. From the isotopic carbon is determined that after plasma and heat exposure: the surface color, surface area and pore volume has been changed. In addition the sample mass is reduced (carbon consumption up to 36% gravimetrically), confirming that carbon is consumed.

This potentially opens a new way toward O_2 removal during CO_2 dissociation processes by combining plasma with heating of carbon to generate a clean CO_2/CO stream. If the carbon is of a biogenic origin, the process as a whole is sustainable and fossil free CO is generated. Other additional processes that aid to further increase the CO yield (like reverse Boudouard reaction: $CO_2 + C \rightarrow 2\,CO$) help to find ways for industry to reach higher CO yields by both increasing the CO_2 conversion and the consumption of O_2 through the presence of carbon via non-thermal plasma.

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4:00pm **PS+AS-MoA-8 Investigation of Oxygen Permeation Enhancement with He/O_2 Plasma and SOEC Interaction***, **Xingyu Chen,*** Dutch Institute for Fundamental Energy Research, China*; F. Peeters, F. Smits, W. Bongers, R. van de Sanden,* Dutch Institute for Fundamental Energy Research, Netherlands

High temperature solid-oxide electrolysis cells (SOECs) using oxygen-selective conducting membrane in combination with plasma has shown high conversion efficiencies in nitrogen fixation and CO_2 conversion, which provides a promising method for renewable energy usage and gas conversion. But the underlying kinetics and limiting rates of the plasma-assisted oxygen conducting membrane remain not clear. The plasma-activated species (e.g., by plasma-excitation, dissociation and ionization) may promote the reduction kinetics on the ion-conducting membrane surface. The effects of plasma-induced surface charging and local fields on the exchange kinetics may also play a significant role in the improvement of the oxygen permeation fluxes of the ion-conducting membrane. To understand the interaction of the plasma and the oxygen-conducting membrane, we develop a dedicated plasma-SOEC reactor to investigate the plasma enhanced oxygen permeation mechanism.

In this contribution, we will present the experimental results of the enhancement of the oxygen permeation fluxes owing to the presence of the oxygen radicals and electrons from He/ O_2 low pressure (~1 Torr) plasma. Langmuir probe measurements and optical emission spectrometry and actinometry will determine the plasma properties (electron density, electron temperature and O radical densities etc.) and provide inputs for the plasma-kinetic modelling of the plasma bulk and wall region. The characterizations of the SOEC with different plasma conditions and membrane temperature are conducted to determine the pumping rates (current density) of the oxygen permeation process. Ultimately, the plasma effects on SOEC performance will be quantified, and novel insights into the ion-conducting rate-limiting kinetics will be discussed.

4:20pm **PS+AS-MoA-9 Application of Plasma-Liquid Chemistry to Carbon-Carbon Bond Formation via Pinacol Coupling Reaction*, Scott Dubowsky*,** *J. Wang,* University of Illinois at Urbana-Champaign*; N. Üner,* Middle East Technical University, Turkey*; J. Moore, M. Sankaran,* University of Illinois at Urbana-Champaign

Low-temperature, atmospheric-pressure plasmas in contact with liquids have attracted interest for various chemical applications including the degradation of organic pollutants,[1] conversion of abundant feedstocks,[2,3] and more recently, organic chemistry.[4] Compared to other chemical approaches, plasma-liquid chemistry does not require a catalyst material, is electrified, and produces unique reactive species such as solvated electrons, one of the strongest chemical reducing species.[5]

We present an application of plasma-liquid chemistry to the building of carbon-carbon bonds via the well-known Pinacol coupling reaction. In this organic reaction, a carbonyl group is reduced, typically by an electron donating catalyst such as magnesium, to form a ketyl radical anion species. A pair of these ketyl groups then react to form a vicinal diol, which in the presence of a proton donor such as water, leads to the final diol product. Here, we show that the Pinacol coupling reaction is successfully carried out at a plasma-liquid interface without any catalyst. Our study was performed with a direct-current (DC) powered plasma operated in a previously reported electrochemical setup and primarily focused on methyl-4-formylbenzoate (MFB) as the substrate. For an initial concentration of 0.12 M and a constant operating current of 2.3 mA, the yield of the Pinacol product increased with time from 6.1% after 1 h to 34% after 8 h, while the faradaic efficiency correspondingly decreased from 85.7% to 54.2%. Based on nuclear magnetic resonance (NMR) spectroscopy, methyl 4-(dimethoxymethyl)benzoate and 4-(methoxycarbonyl)benzoic acid were also generated as side products. By carrying out scavenger control experiments, we show that the vicinal diol is produced by solvated electron reduction. Finally, we have extended the application of plasma-liquid chemistry to Pinacol coupling of several other aromatic aldehydes and ketones to emphasize its generality.

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4:40pm **PS+AS-MoA-10 Understanding Temperature Inhibition of Methane Conversion in DBD Plasma Using Electrical Characterization and Optical Emission Spectroscopy*, Ibukunoluwa Akintola,*** *G. Rivera-Castro, J. Yang, J. Hicks, D. Go,* University of Notre Dame

Non-thermal plasmas (NTPs) produce highly reactive chemical environments made up of electrons, ions, radicals, and vibrationally excited molecules. These reactive species, when combined with catalysts, can help drive thermodynamically unfavorable chemical reactions at low temperatures and atmospheric pressure. We are particularly interested in the direct coupling of light hydrocarbons (e.g. methane) and nitrogen to produce value-added liquid chemicals (e.g. pyrrole and pyridine) in a plasma-assisted catalytic process. In order to effectively create these plasma catalytic systems, it is imperative that there is a fundamental understanding of the plasma-phase chemistry alone. While there have been many studies on nitrogen (N_2) and methane (CH_4) plasmas, there is limited understanding on how changing operating conditions (i.e. feed ratio, plasma power, operating temperature) affect the plasma properties and ensuing plasma chemistry. In this work, we characterize the plasma using electrical measurements and optical emission spectroscopy (OES) and analyze the chemical products using gas chromatography to understand the effects, if any, of varying plasma parameters on product formation. Relevant electrical properties and thermodynamic information such as electron density, vibrational and rotational temperatures, as well as the presence of key plasma species (C-N, C-H, N_2) are compared to relevant products formed during plasma-alone reactions. Results show that different operating conditions lead to changes in energy partitioning in the reaction. Specifically, an increase in temperature leads to a reduction in methane conversion which appears to have an inverse relationship with the vibrational temperatures of C-H species in the plasma.

5:00pm **PS+AS-MoA-11 Optimization of CO_2 Dissociation Efficiency and Conversion in Vortex-Stabilized Microwave Plasmas by Effluent Nozzles*, Cas van Deursen,*** DIFFER, Netherlands*; H. van Poyer,* DIFFER, Belgium*; Q. Shen,* DIFFER, China*; W. Bongers,* DIFFER, Netherlands*; F. Peeters,* Technical University of Eindhoven, Netherlands*; F. Smits, R. van de Sanden,* DIFFER, Netherlands

Efficiency and conversion in a reverse vortex microwave plasma utilized for CO_2 dissociation are enhanced by considering and optimizing the thermal trajectory of the plasma effluent using a Laval nozzle. The nozzle is used to mix the cold, unconverted gas at the edges of the tube with the hot, dissociated gas in the middle of the flow and to force the gas to accelerate, thereby cooling the effluent. The temperature trajectory of the gas is determined by measuring the gas temperatures of the plasma core and the afterglow using OES and the gas exiting the Laval nozzle using a thermocouple. The effects of the nozzle on the size of the plasma is determined using OES and plasma imaging. The effects of different nozzle diameters on the temperature trajectory and conversion and efficiency are compared to the baseline configuration. Measurements show significant improvements in energy efficiency at close to atmospheric pressures (500 – 900 mbar), especially for higher flows (12 – 18 slm). Results are discussed and explained on the basis of simulations. Options for further improving reactor efficiency and conversion are also discussed.

Surface Science Division
Room 319 - Session SS+AS-MoA

Molecular Organization at Surfaces

Moderator: Donna Chen, University of South Carolina

2:40pm **SS+AS-MoA-4 Protein Structure and Dynamics at the Air-Water Interface Using Sum Frequency Generation Simulations*, Kris Strunge,*** Aarhus University, Denmark*; Y. Nagata,* Max Planck Institute for Polymer Research, Germany, Denmark*; T. Weidner,* Aarhus University, Denmark

Protein function and folding are perturbed by the presence of interfacial environments. Many protein is active at an interface making it most relevant to study these molecular systems right at the interface. However, the study of the topmost monomolecular layer is made difficult by the high of amount of solvated protein in close proximity to the interesting interfacial species. This calls for spectroscopic methods like sum frequency generation (SFG) spectroscopy, which is inherently surface sensitive from its selection rules and allow studies of the molecularity at the interface based on the vibrational spectrum coming specifically from the interface probing molecular orientation, structure dynamics and interactions. However, extracting this information from the SFG spectrum a challenge due to the non-linear phase sensitive interference affecting the spectrum which can be solved by relating experimental SFG spectra with accurate spectra calculation based on molecular simulation.Wewant to show how information from SFG spectroscopy can be coupled with molecular dynamics simulation to resolvemolecular orientation, dynamics and interactions of proteins at interfaces.

The sum frequency spectrum of the LTα14 peptide shows a characteristic amide I peak at 1640 cm^{-1}signifying the expected α-helical structure, but more specific informationlike interactions with per residueresolution and the nature of their vibrations at the interface is gained bycalculating the SFG spectrum based on state-of-the-art velocity-velocity time correlation functions sampled through molecular dynamics simulation. With this tool we can learn how the frequencies of each individual amino acid residue contributions and inter-residue coupling lead to the inhomogeneous broadening of the surface specific vibrational spectrum. For example, we can learn thatα-helical peptides lying flat on an interface mainly interacts withsurface withthe residues on the side of the helix. The top and bottom positioned residues are more rigid and despitethe bottom residues' close proximity to the surface, they are not as highly perturbed by the presence of the interface.

Furthermore, SFG allowsus to probe the influence of interfacial proteins on the water structure and the vibrational response of interfacial water as the spectra simulations is easily transferred to other molecular systems of interest in the scientific community.

3:00pm **SS+AS-MoA-5 Confinement at Solid-solid Interfaces Enhances Crystallinity of COF Thin Films***, **Joshua Roys**[1], J. O'Brien, N. Stucchi,* Clarkson University*; A. Hill,* St. Lawrence University*; J. Ye, R. Brown,* Clarkson University

The condensation reaction of covalent organic frameworks (COFs) on the mica surface demonstrated enhanced crystallinity when physically confined by an exfoliated graphene capping layer. This talk discusses the impact of confinement at a solid-solid interface on two-dimensional COF growth at the solid-solid interface. Understanding confined COF behavior could inform new applications, such as the integration of 2D COFs into 2D van der Waals materials as intercalated layers. The growth of 2D COFs was characterized at the mica-graphene interface by atomic force microscopy (AFM), micro-Fourier transform infrared spectroscopy (micro-FTIR), and density functional theory (DFT). At temperatures sufficient for reaction, AFM topographic and phase imaging observed long-range crystalline growth on the order of square micrometers in graphene-confined domains. Domains outside of the exfoliated graphene flakes did not exhibit long-range mesoscale structural order and retained similar morphology to pre-annealed structures. Micro-FTIR spectra confirmed COF formation both under and outside graphene confinement, as well as an increased presence of trapped water beneath graphene after reactive annealing. Diffusion barriers estimated by DFT calculations suggested the enhanced crystallinity of confined COFs was not the result of heightened mobility of confined molecules or non-covalent self-assembly. The increased COF crystallinity when confined by a graphene layer most likely originated from enhanced dynamic covalent crystallization due to prolonged exposure to water trapped beneath the graphene flake during the annealing process. This behavior should be universal for condensation-reaction covalent organic frameworks formed under confinement at solid-solid interfaces.

3:20pm **SS+AS-MoA-6 Metal Tetraphenylporphyrin Induced Organic/Metal Interactions***, **Isheta Majumdar**, F. Goto, A. Calloni, M. Finazzi, L. Duò, F. Ciccacci, G. Bussetti,* Politecnico di Milano, Italy

The field of organic electronics has seen the emergence of engineered hybrid metal electrode/organic molecule interfaces where molecules can be ordinally assembled in 2D scalable devices. Metal surfaces can be screened (passivation) by single atomic layers, namely, ultra-thin metal oxide layers, in view of preserving the molecular electronic properties when deposited on the underlying substrate [1].

In the present work, one such system studied is the passivated iron, known as Fe(001)-*p*(1 × 1)O (preparation protocol in [2]), with a metal tetraphenylporphyrin (MTPP) overlayer deposited under ultra-high vacuum, using a molecular beam epitaxy system. The sample is characterized by ultraviolet photoelectron spectroscopy (UPS) and low energy electron diffraction (LEED). We have observed that transition MTPP (M= Co, Ni, Pt, Pd) deposition on Fe(001)-*p*(1 × 1)O have resulted in the same *commensurate* (5 × 5)R37° superstructure (37° rotation w.r.t. the main Fe crystal), as observed by LEED pattern. ZnTPP and CdTPP are the only exceptions, which exhibit regular (5 × 5) symmetries, while Fe(Cl)TPP and CuTPP show mixed LEED patterns (presence of overlapping regular and rotated superstructures). This occurrence drove a detailed investigation to find possible strategies (surface engineering) to obtain a specific molecular superstructure.

Therefore, in the next phase of our study, mixed M$_1$TPP + M$_2$TPP monolayers were grown sequentially at room temperature by depositing *x* ML of M$_1$TPP on Fe(001)-*p*(1 × 1)O followed by (1-*x*) ML of M$_2$TPP (Fig. 1). The corresponding UPS characterization (Fig. 1 (i)) confirms the monolayer coverages of the mixed MTPP layers. In Fig. 1 (ii), top row: CoTPP (M$_1$TPP) is deposited first (*x* = 0.25), followed by ZnTPP; bottom row: ZnTPP (M$_1$TPP) is deposited first (*x* = 0.25), followed by CoTPP. It is observed that the growth of a CoTPP "seed" is able to stabilize a ZnTPP (5 × 5)R37° ordering, not observed on a pure ZnTPP layer. Conversely, a ZnTPP "seed" results in a mixed LEED pattern, where CoTPP molecules retain their characteristic (5 × 5)R37° ordering. This occurrence indicates that there is a significant influence of one type of MTPP over the other that determines the surface reconstruction.

Furthermore, in another set of mixed MTPP depositions, nominally equal amounts of ZnTPP and CoTPP where grown by means of co-deposition on Fe(001)-*p*(1 × 1)O. In this case, CoTPP showed a certain dominance while influencing the resultant surface reconstruction of the mixed MTPPs. 0.50 ML CoTPP and 0.50 ML ZnTPP co-deposition resulted in a (5 × 5)R37° ordering (Fig. 1 (iii)).

4:40pm **SS+AS-MoA-10 Characterization of Oxygen Evolution from Rh(111)***, **Maxwell Gillum**, E. Jamka, C. Grytsyshyn-Giger, F. Lewis, A. Kerr, D. Killelea,* Loyola University Chicago

Due to the importance of oxide surfaces in heterogeneously catalyzed reactions, it is critical to gain a fundamental understanding of the reactivity and behavior of oxygen on these transition metal surfaces. In previous studies we have been able to establish that the reactivity and thermodynamic stability of oxygen on Rh(111) relies in part on the concentration of oxygen present in the subsurface. However, more research needs to be conducted in order to gain a better understanding of the relationship between surface reactivity and subsurface concentration. In addition to the techniques used in our previous studies, namely temperature programmed desorption (TPD) and scanning tunneling microscopy (STM), the experiments herein will include simultaneous infrared (IR)/TPD techniques to gain more information on these critical interactions.

5:00pm **SS+AS-MoA-11 Developing a Mechanistic Understanding of Nb_3Sn Growth: Sn Adsorption and Diffusion Behavior on (3×1)-O Nb(100)***, **Rachael Farber**,* University of Kansas*; S. Willson,* University of Chicago*; A. Hire, R. Hennig,* University of Florida*; S. Sibener,* University of Chicago

Niobium (Nb) is the current standard material for superconducting radio frequency (SRF) accelerator cavities due to its ultra-low surface resistance and high cavity quality factor (*Q*) at operating temperatures of ~ 2 K. The prohibitively expensive operating and infrastructure costs of these facilities prevent the implementation of accelerator-based technologies across a variety of sectors. Nb_3Sn is a promising next-generation material for SRF cavities due, in part, to an elevated operating temperature of ~ 4.2 K.This significantly reduces the required cryogenic infrastructure and associated operating costs.

Nb_3Sn films are currently grown *via* Sn vapor deposition on preexisting Nb cavities. It is understood that the thickness of the native Nb pentoxide (Nb_2O_5), Sn homogeneity, surface roughness, and alloy thickness must be well controlled for high *Q* film growth.There is not, however, an understanding of the Nb_3Sn growth mechanism resulting in optimal film formation. In this work, we have used a combination of *in situ* ultra-high vacuum (UHV) techniques to visualize Sn adsorption and diffusion behavior on (3×1)-O Nb(100) at the nanometer scale. Scanning tunneling microscopy (STM) data revealed preferential adsorption of Sn along the (3×1)-O unit cell with Sn diffusion guided by the underlying oxide surface as well. Annealing the Sn/Nb(100) sample resulted in the formation of hexagonal and rectangular Sn adlayer structures for all sub-monolayer (sub-ML) and ML Sn coverages studied. Genetic algorithm calculations and DFT based descriptors identified energetically preferred Sn binding sites on the (3×1)-O surface.Calculated STM images corroborated experimentally determined Sn adsorption structures for sub-ML Sn coverages. This spatially resolved, mechanistic information of Sn adsorption and diffusion on an oxidized Nb surface guides the development of predictive Nb_3Sn growth models needed for the further optimization of Nb_3Sn growth procedures.

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[1] **SSD Morton S. Traum Award Finalist**

Thin Films Division

Room 316 - Session TF+EM-MoA

Thin Films for Optics, Photonics, Metamaterials, and Soft Electronics

Moderator: April Jewell, Jet Propulsion Laboratory

1:40pm **TF+EM-MoA-1 Strategies for Achieving Tunable Infrared Emission in III-V Materials***, **Michelle Povinelli**, H. Chae, A. Ghanekar, B. Shrewsbury, R. Ahsan, R. Kapadia,* University of Southern California **INVITED**

We investigate strategies for creating tunable thermal emitters in III-V platforms. Two fabrication approaches are examined: direct growth of III-V films on metallic substrates and epitaxial transfer. We design corresponding infrared metamaterials and measure their wavelength-dependent absorptivity using FTIR spectroscopy. We demonstrate electrically induced shifts in the absorptivity spectrum. We then introduce device designs for absorptive/emissive switching. We assume that the applied voltage induces a perturbative index shift with double the period of the initial metamaterial. With careful design, the perturbation is predicted to switch the thermal emission on and off within a specified bandwidth and angular range.

2:20pm **TF+EM-MoA-3 Effects of Ultra-Thin Conformal Coatings on the Spectral Location of Reciprocal Plasmonic Metasurface Resonances***, **Micheal McLamb**, V. Stinson, N. Shuchi, G. Boreman, T. Hofmann,* University of North Carolina at Charlotte

Optical metamaterials are a group of engineered materials that are composed of an arrangement of artificial structures, which result in properties that are not exhibited in naturally occurring compounds. These unique optical properties can be used to produce extraordinary optical effects including narrow band filtering [1], perfect lensing [2], and perfect absorption [3].

In order to achieve perfect absorption, metamaterial designs that rely on heterostructures have shown promising results [3, 4]. Heterostructured materials are composed of multiple, stratified constituents. We have developed a reciprocal plasmonic metasurface that is composed of two plasmonic metasurfaces with reciprocal surface geometries that are separated by a dielectric spacer. Experimental infrared reflection measurements revealed the expected reciprocal plasmonic metasurface resonance, which was observed for the investigated geometries, at 4.8 µm. The location of this resonance was in agreement with finite element calculations.

We have also explored the optical response of reciprocal metasurfaces when coated with a conformal dielectric, amorphous Al_2O_3, for different coating thicknesses: 10 nm, 20 nm, 30 nm, and 40 nm. In order to experimentally explore the effect of ultra-thin conformal dielectric coatings on the spectral location of the reciprocal plasmonic metasurface resonance, Al_2O_3 coatings were deposited using atomic layer deposition. Our observations indicate that such dielectric coatings can induce a spectral red-shift of the main resonance of the reciprocal plasmonic metasurface allowing for the tuning of the resonant frequency.

1. V.P. Stinson, S. Park, M. McLamb, G. Boreman, and T. Hofmann, Optics, **2**, 284-291 (2021).
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2:40pm **TF+EM-MoA-4 Integrating Structural Colors with Additive Manufacturing Using Atomic Layer Deposition***, **Tae Cho**, B. Rorem, N. Farjam, J. Lenef, K. Barton, J. Guo, N. Dasgupta,* University of Michigan, Ann Arbor

Structural colors, which allow for tunable surface reflectance spectra, are being increasingly used in a variety of applications such as optical displays, prints, decorations, and color photovoltaics. Compared to pigment-based colors, structural color offers many advantages including high brightness, durability, environmental sustainability, and ease of fabrication. However, traditional thin-film deposition processes often suffer from conformality, thickness control, and versatility in material selection. Compared to these techniques, atomic layer deposition (ALD) offers unparalleled control of film thickness and uniformity on complex topologies at relatively low temperatures which is compatible with polymer/biological/organic substrates. In this work, we fabricated asymmetric metal-dielectric-metal (MDM) structures which were sequentially deposited with nickel, zinc oxide (ZnO), and copper layer to form optical cavities. The ZnO thickness was varied from 40 nm to 160 nm which exhibited a full-color cycle from red, blue, and to yellow which agreed with the simulated spectra using the transfer matrix method.

To demonstrate the power of ALD to enable uniform and tunable coloration of non-planar three-dimensional objects, ALD MDM structures were deposited on 3-D printed metal objects. Blue and yellow colors were 'painted' onto the 3-D printed surface using 80 nm and 120 nm thick ALD ZnO, respectively, with 20 nm thick copper top layer. Vibrant and uniform colors were observed across all of the curved features owing to ALD's conformal coating of the microscopic porous topologies from metal 3-D printing.

Furthermore, our previous work has shown that using electrohydrodynamic jet (e-jet) printing, we can locally activate/passivate ALD growth for area-selective ALD (AS-ALD) patterning down to approximately 300 nm resolution [1]. By using e-jet printed patterns to control AS-ALD, multiple colors were printed on the same substrate by patterning the polymer inhibitor layers. This enables color printing of functional ALD materials with resolutions well below that of ink-jet printing. By combining AS-ALD with structural color, this work can open up the possibility of integrating additive nanomanufacturing with structural colors into even more complex 3-D geometries including hierarchical architectures that span nano- to macro-length scales.

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3:00pm **TF+EM-MoA-5 Biosensor Encapsulation via Photoinitiated Chemical Vapor Deposition (piCVD)***, **Ruolan Fan**, T. Andrew,* University of Massachusetts - Amherst

Thin and porous poly(hydroxyethyl acrylate) (pHEA) and poly(3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooctyl acrylate) (pTFOA) encapsulating layers were successfully deposited on model electrical and optical glucose sensors via photoinitiated chemical vapor deposition (piCVD). This surface-restricted chain growth process afforded uniform coverage and strong interfacial adhesion of the resulting polymer encapsulation layers, which enabled the whole sensing area to be fully covered, even after being subjected to numerous electrochemical scanning cycles. Meanwhile, the amorphous films allowed rapid ion and analyte diffusion through themselves and, therefore, achieved quick sensing responses. Especially, pTFOA promised well-defined calibration curves with good repeatability. Furthermore, piCVD films maintained their morphology after being dehydrated and rehydrated over multiple days demonstrating their excellent stability as surface protective layers. These promising features of pHEA and pTFOA synthesized via piCVD may serve as a new encapsulating idea to be applied to various wearable sensors with different substrates and serve as a new strategy to extend the shelf life and functionality of biosensors.

3:20pm **TF+EM-MoA-6 Harnessing Wide-Range, Highly Stable Pressure Sensitivity Via PEDOT-Cl Vapor Printed Textiles for Health Monitoring***, **S. Zohreh Homayounfar**, A. Kiaghadi, D. Ganesan, T. Andrew,* University of Massachusetts, Amherst

The advancement of wearable electromechanical sensors to detect biopotentials and body locomotion is critically important in evaluating human performance and improving off-site care applications. The practicality of most of the so-far-developed sensors is highly restricted by the small range of detection and low stability against aging phenomena such as cycling abrasions, exposure to perspiration, and washing. By vapor deposition of a p-doped conjugated polymer, poly(3,4-ethylene dioxythiophene): chloride (PEDOT-Cl), we introduce an ultra-stable pressure sensor that reveals high sensitivity in detecting real-time signals in such a wide range of pressures that have not been reported before (from heartbeats to more than bodyweight). We leveraged a multi-scale working mechanism by developing two sensors: one with PEDOT-Cl coated cotton fabric and one with PEDOT-Cl coated cotton ball as the active layer. In addition to having percolation on the microscale, our sensors harness piezoionic effect on the nanoscale, which means that the redistribution of ions under the applied mechanical stress leads to the change in resistance. We protected the sensor against all the humidity-induced degradations entangled with ions and other aging processes via vapor deposition of hydrophobic moieties on all the sensor layers. With this protective coating, the sensor shows less than no change in resistance and sensitivity after staying in ~100% humidity for more than 150 hrs and can stand more than 10 laundry cycles without any drop in signal quality. Also, it displays ultra stability with 99.1% over 70,000 bending cycles in ambient conditions. The broad ability of this sensor was further confirmed by acquiring physiological signals and body motions such as heartbeats, respiration, and Joint movements. All these properties, along with the low-cost and robust fabrication process, bear the testimony that this sensor will be uniquely placed in wearable health monitoring electronics for both diagnostic and treatment applications.

Vacuum Technology Division
Room 301 - Session VT-MoA

Vacuum Technology for Accelerators

Moderators: Giulia Lanza, SLAC National Accelerator Laboratory, **Yevgeniy Lushtak**, SAES Getters USA

1:40pm **VT-MoA-1 Developments of the Vacuum Systems Required for the Electron Ion Collider*, Charles Hetzel,*** Brookhaven National Laboratory **INVITED**

The Electron-Ion Collider (EIC) is a new particle accelerator which collides electrons (10 GeV, 2.5A) with protons (275 GeV, 1.0A) and nuclei that will be constructed at Brookhaven National Laboratory in the coming decade. This new machine will utilize the most of the existing infrastructure and accelerator complex of the currently operating Relativistic Heavy Ion Collider (RHIC). The hadron storage ring (HSR) will reuse some of the two superconducting RHIC storage rings. An electron storage ring (ESR) will be installed in the existing RHIC tunnel to provide electrons for beam collisions with the HSR hadron beam in up to two interaction regions. Fully polarized electron bunches will be injected to the ESR at fully energy (up to 18GeV) by a rapid-cycling synchrotron (RCS) which will also be constructed in the same accelerator tunnel. In order for this complex to reach its fully envisioned potential (luminosity of 10^{34} $cm^{-2}s^{-1}$), many new and challenging vacuum systems, including more than 8km of new UHV beam pipes as well as many upgrades to the existing storage rings will be required. During this presentation, I will be providing a brief overview of the various vacuum systems as well as some of the many challenges which need to be overcome.

2:20pm **VT-MoA-3 Vacuum System of the MAX IV 3 GeV Storage Ring: Design and Performance*, Marek Grabski,*** *M. Grabski,* Max IV Laboratory, Sweden **INVITED**

MAX IV 3 GeV storage ring is the first synchrotron light source implementing compact multi-bend achromat (MBA) magnet lattice and vacuum system fully coated with non-evaporable getter (NEG). The storage ring is in operation for over 6 years, providing ultra-low electron beam emittance and delivering photon beams to beamlines from insertion devices.

The storage ring vacuum system, based on the NEG coating, proved to be reliable and has very good performance. The total average pressure is below 1e-9 mbar and is reducing with the accumulated beam dose since the start of the operation. The total electron beam lifetime of approximately 5 Ah is not limited by the vacuum related beam lifetime which is greater than 39 Ah.

Several successful installations were accomplished on the storage ring during shutdowns. Some interventions were performed utilizing purified Neon venting to avoid re-activating of the NEG film, thus saving installation time without compromising the accelerator performance.

Design principles, performance and operational status of the 3 GeV storage ring vacuum system will be presented.

3:00pm **VT-MoA-5 Fabrication and Assembly Status of the APS-Upgrade Storage Ring Vacuum System*, Jason Carter,*** *O. Mulvany, G. Wiemerslage,* Argonne National Laboratory

The Advanced Photon Source Upgrade (APS-U) project is progressing towards the coming dark time for APS and installation and commissioning of the new storage ring including a new vacuum system. Vacuum system design is complete and procurements and vacuum chamber production is underway for over 2400 vacuum chambers, absorbers, and beam position monitors as well as supplemental hardware. A pre-assembly phase of vacuum system and magnet modules has begun in the summer of 2022. A total of 200 modules, 5 each per 40 sectors, will be installed in the APS-U storage ring. This presentation will fabrication status of the various vacuum components, the status of vacuum system assembly, and the challenges ahead. Challenges include installation within restricted space access, preventing UHV contamination, achieving precision alignment goals, and protecting sensitive components such as thin-walled vacuum chambers, bellows, and delicate RF liners while maintaining progress in a heavy-duty assembly area.

4:00pm **VT-MoA-8 CW Superconducting Linac for the LCLS-II HE Free Electron Laser at SLAC*, Marc Ross,*** SLAC National Accelerator Laboratory **INVITED**

This year the X-ray Free Electron Laser 'LCLSII', will start commissioning activities. LCLS-II (Linac Coherent Light Source - II) is a photon science user facility that produces ultra-short very high peak-power narrow-band X-ray pulses, up to a million pulses per second and up to 5 keV photon energy. The facility is used primarily for applied science, including for example molecular biology, matter in extreme conditions, and engineered materials. The high repetition rate and ultra-short pulses will allow scientists to make stop-action movies at atomic scales.

The heart of the facility is a new CW 4 GeV superconducting electron linac based on the well-developed 1.3 GHz TESLA technology. The linac consists of 37 Cryomodule units that house 296 nine-cell niobium cavities operating submerged in superfluid liquid helium at 2 Kelvin. A major advancement is the monolithic nature of the linac with the cryomodules directly connected to each other to make a ~ 100 meters long cryogenic volume. It is believed this advancement helps keep contaminants such as particulates and organic chemicals away from the RF cavity vacuum volume, and it is acknowledged Cryomodule exchange is more difficult. No getters or ion pumps are used in the long cryomodule string.

This is the first superconducting linac to be constructed using niobium cavities that have their surface doped with nitrogen. This recent innovation makes the superconductor 3 to 4 times less resistive and allows the entire facility to fit within the capacity of a single liquid helium cryoplant. The doping is carried out by the cavity vendors at the end of the high temperature degas vacuum bake. The doped cavity production run ended in 2019 with excellent performance results.

Assembling the cryomodules and integrating them in the accelerator enclosure tunnel requires the best available particulate and contamination control. It is believed that a single ~micron sized particle or contamination-spot near the high voltage iris of the accelerator cavity will substantially degrade its voltage performance. Following pioneering work at the Oak Ridge Spallation Neutron Source, we plan to deploy a chemically-active plasma processing technique.

In 2020 SLAC and its partners, Fermilab and Jefferson Lab, embarked on an upgrade project called LCLS-II-HE to extend the capability of the linac from 4 to 8 GeV. The upgraded linac will be 1 km long and will be complete in 2027. In this presentation we will show the application of accelerator technology to the ultra-high performance LCLS-II-HE CW superconducting linac.

4:40pm **VT-MoA-10 Upgrades for the Jefferson Lab Injector and Linac Accelerator Vacuum Systems*, Marcy Stutzman,*** Thomas Jefferson National Accelerator Facility

The accelerator vacuum systems at Thomas Jefferson National Accelerator Facility (Jefferson Lab) were initially designed in the 1980s. Over the past several years, the injector beamline vacuum has been upgraded during the first phase of the injector upgrade, and more improvements are planned for the upcoming phase 2 work. Enhanced pumping has also been implemented in the warm girders between the accelerator cryomodules as they are refurbished and replaced in the linacs. I will describe the competing factors for the accelerator vacuum, including the implementation of improved pumping and materials processing for the injector upgrade and quantify the operational results of the enhanced vacuum system. Additionally, I'll describe the goals of the upgrades to the warm girders in the linacs, and compare performance between the zones with added NEG pumping compared to the legacy zones.

5:00pm **VT-MoA-11 Vacuum Leak Detection with Variational Smoothing for Vacuum Process Chamber***, **Taekyung Ha**,* PSK, Republic of Korea

Fault detection is an important method in semiconductor manufacturing for monitoring equipment condition and examine the potential causes of the fault. The vacuum leakage is considered one of major fault in semiconductor processing. Unnecessary O_2, N_2 mixture, major components of atmosphere, creates unexpected process results hence drops yield. Currently available vacuum leak detection systems in vacuum industry are based on helium-mass spectrometers. It is used for detecting the vacuum leakage at sole isolation condition where chamber is fully pumped, but unable to use at in-situ detection condition that while process is on-going in the chamber. In this study, a chamber vacuum leak detection method named variational smoothing autoencoder has been presented, utilizing common data which gathered during normal chamber operation. This method was developed by analyzing a simple list of data, such as temperature of the chamber body and the position of auto pressure control (APC) to detect any change of leakages in the vacuum chamber.

The weakest point of data smoothing is the loss of information. To improve this problem, a variational smoothing method was developed. The length of the process log data is slightly different for each process due to the limit of command processing according to the sequence of the computer. To improve this problem, we partition the time series data and extract the segment information. The extracted segment information is strongly related. So, the autoencoder model was applied to train well on highly relevant data. The proposed method, variational smoothing autoencoder model, showed the best performance, area under the ROC curve (AUC) by 0.84 and accuracy by 0.76. Variational smoothing autoencoder were effective in classifying abnormalities by predicting time series data of semiconductor facility sensors.

Atomic Scale Processing Focus Topic
Room 317 - Session AP+AS+EM+HI+PS+SS+TF-TuM

Area Selective Processing and Patterning II

Moderators: Michelle Paquette, University of Missouri-Kansas City, **Christophe Vallee**, SUNY College of Nanoscale Science and Engineering

8:00am **AP+AS+EM+HI+PS+SS+TF-TuM-1 New Precursors and Approaches to ALD and AS-ALD of Metals*, Mikko Ritala,*** University of Helsinki, Finland **INVITED**

Metal ALD is a topic where high technological relevance combines with inspiring and challenging scientific questions. As always, the success of ALD builds on chemistry. There is constant need for new precursors enabling ALD of metals of interest with improved characteristics. A major challenge arise from the strong tendency of metals to agglomerate, hence preventing achieving continuous films at the smallest thicknesses. Lowering of the deposition temperature is of utmost importance to limit the agglomeration. This requires highly volatile and reactive metal precursors and reducing agents. 1,4-bis(trimethylgermyl)-1,4-dihydropyrazine ($(Me_3Ge)DHP$) is a new reducing that is found more efficient than its earlier reported silicon analogue. $NiCl_2(PEt_3)_2$ in turn represents a series of metal halide adduct compounds of nickel and cobalt where the poorly volatile parent halides are made volatile by proper adduct ligands. The $NiCl_2(PEt_3)_2$ - $(Me_3Ge)DHP$ combination affords deposition of Ni at 110 °C which is the lowest temperature for thermal ALD of Ni so far. $(Me_3Ge)DHP$ enables also deposition of gold. This is the first reductive thermal ALD process of gold.

Area-selective ALD of metals is an important topic for self-aligned thin-film patterning. An entirely new approach to this is area-selective etching of polymers. In these etching processes the selectivity arises from the materials underneath the polymer layers. Both O_2 and H_2 can be used as an etchant gas. Etching gas molecules diffuse through the polymer film, and if they meet a catalytic surface underneath, the molecules become dissociated into their respective atoms which then readily react with the polymer etching it away. On noncatalytic surfaces the polymer film remains. When combined with area-selective ALD, self-aligned etching of polymers opens entirely new possibilities for the fabrication of the most advanced and challenging semiconductor devices. An example is given where the area-selective etching of polyimide from Pt was followed by area-selective ALD of iridium using the patterned polymer as a growth-inhibiting layer on SiO_2, eventually resulting in dual side-by-side self-aligned formation of metal-on-metal and insulator (polymer)-on-insulator.

8:40am **AP+AS+EM+HI+PS+SS+TF-TuM-3 Comparing Interface and Bulk Physicochemical Properties of TiO_2 Deposited by PEALD Assisted by Substrate Biasing on Thermal SiO_2 and TiN Substrates, for Area Selective Deposition Application*, Jennifer Not,*** LTM - MINATEC - CEA/LETI, France*; L. Mazet,* STMicroelectronics, France*; T. Maindron,* Minalogic, France*; R. Gassilloud,* CEA-LETI, France*; M. Bonvalot,* LTM - MINATEC - CEA/LETI, France

To bypass the limitations implied by the miniaturization of electronic components, area selective deposition (ASD) is becoming a key point of focus, as photolithography steps are avoided. This bottom-up promising technique, as opposed to the top down approach inherent to etching, relies on nucleation mechanisms resulting from substrate - precursor interactions. Differing nucleation kinetics may indeed be observed under very same experimental conditions,[1] allowing a growth delay on a surface type while simultaneously promoting growth on a different surface.

Atomic Layer Deposition (ALD) remains a technique of choice to obtain area selective deposition. Based upon the self-limiting nature of surface reactions, this technique enables a conformal deposition with atomic-scale thickness precision, and is gradually becoming a major deposition process in the microelectronic industry.

The ALD reactor used in this study includes an ICP deported plasma source and is equipped with an additional RF polarization kit at the back side of the chuck, enabling plasma ion extraction from the source towards the substrate surface. Depending on the ion incident kinetic energy, which can be tuned as a function of the applied polarization bias, this ion flux can modulate the properties of the thin film under growth, opening new perspectives of physicochemical properties. These properties may also vary according to the substrate surface, making this RF polarization kit an interesting experimental knob for the development for ASD processes[2].

PEALD TiO_2 layers of various thicknesses have been deposited with no air break on a 15 nm-thick TiN layer, as well as on a 100 nm-thick thermal SiO_2 substrate, under various polarization bias power from 0 W to 80 W. The purpose of this work is to physically and chemically characterize the obtained thin films with respect to substrate surface, and to understand how these properties evolve with the film thickness and for various bias values. X-Ray Reflectivity (XRR), Grazing Incident X-Ray Diffraction (GIXRD), *in-situ* and *ex-situ* ellipsometry and Angle Resolved X-ray Photoelectron Spectrometry (AR-XPS) measurements have been performed, providing detailed information on chemical bond formation during nucleation and within the bulk TiO_2 layer, and thin film physical properties, such as thickness, density, roughness and crystallinity. The outcome of this study gives some insight into the benefit of bias for area selective deposition of TiO_2 thin films on TiN against SiO_2.

References

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17. T. Faraz *et al*., ACS Appl. Mater. Interfaces, 10, 13158−1318 (**2018**)

9:00am **AP+AS+EM+HI+PS+SS+TF-TuM-4 Area Selective Atomic Layer Deposition of SnO_2 as An Etch Barrier*, Xin Yang,*** University of Texas at Austin*; B. Coffey,* Lam Research Corp*; J. Ekerdt,* University of Texas at Austin

Reactive ion etching (RIE) is widely used in semiconductor nanofabrication processes since it can provide high etch rate, high selectivity, and high anisotropy. Traditional etch masks such as organic photoresists suffer from shortcomings such as low etch selectivity. Other material systems have been investigated to improve the selectivity. $Sn^{(0)}$-containing block copolymers were demonstrated as materials for nanolithographic applications.

Here we propose SnO_2 as a RIE etch mask in fluorine-based etching processes. Tin forms nonvolatile compounds with fluorine enabling tin to function as an etch mask. We establish processes that create SnO_2 grid patterns, which can be transferred into the Si native oxide substrate using SF_6 RIE. The concept is illustrated using a 1000-mesh copper TEM grid as an ultraviolet light shadow mask to generate patterns in polystyrene. SnO_2 patterns are achieved by area selective atomic layer deposition (ALD) using tetrakis(dimethylamino) tin(IV) and H_2O as ALD precursors on a Si native oxide at 170 °C. The selective growth can be directed by the hydrophilicity of the substrate surface. ALD growth of SnO_2 shows no nucleation delay on Si native oxide, which is hydroxylated. By coating the substrate with a polymer such as polystyrene (PS) the reactive sites can be passivated to accomplish selective growth. SnO_2 growth can be blocked up to 50 cycles on H-terminated Si(001), and 200 cycles on cured polystyrene and possibly beyond. Atomic force microscopy (AFM) results show that SnO_2 grown on native oxide has a low roughness of 75 pm, while SnO_2 grown on H-terminated Si has a relative higher roughness of 250 pm indicating a 3-D growth process. To create SnO_2 patterns 20, 50, and 100 ALD cycles of SnO_2 are selectively deposited onto Si native oxide with estimated SnO_2 thicknesses of 1.2 nm, 3 nm and 6 nm, respectively. Samples are then etched with SF_6 RIE for 30 s to 1 min at room temperature and 200 mTorr. AFM results show that SnO_2 grid patterns are transferred into the substrate with a depth of around 300 nm to 1 µm for all three samples. X-ray photoelectron spectroscopy results show that some SnO_2 is transformed into SnF_4 for 100 ALD cycle samples, while all of the SnO_2 is transformed into SnF_4 for 20 and 50 ALD cycle samples.

9:20am **AP+AS+EM+HI+PS+SS+TF-TuM-5 Selective Deposition Two Ways: Chemical Bath Deposition of Metal Sulfides on Organic Substrates***, T. Estrada,* ***Amy Walker,*** University of Texas at Dallas

Selective deposition has many technological applications. While area selective deposition (ASD) has been widely investigated using atomic layer deposition (ALD), there have been few studies of composition-selective deposition or ASD in which growth occurs at material boundaries. In this talk we shall illustrate these alternate selective deposition methods using two examples.

First, we demonstrate that the composition of tin sulfides is controlled by the bath pH and the interaction of sulfur-containing species with $-CH_3$, -OH and -COOH terminated self-assembled monolayers (SAMs). On -OH terminated SAMs, as the bath pH increases from 10 to 12, the tin sulfide deposited changes from SnS_2 to Sn_2S_3. On -COOH terminated SAMs the deposit is S_2S_3 at pH 10 and SnS at pH 12. In contrast, on -CH_3 terminated SAMs the deposit changes from SnS at pH10 to Sn_2S_3 at pH 12. We attribute this behavior to a competition between the repulsion of the chalcogenide ions by the negatively charged carboxylic acid and hydroxyl terminal groups and an increase in chalcogenide ion concentration with increasing bath pH.

Second, we exploit the interaction of the chalcogenide ions with different SAM terminal groups to deposit CuS nanowires at the junction of micropatterned -OH/-CH_3 terminated SAMs. We term this method SEmiconductor Nanowire Deposition On Micropatterned substrates (SENDOM). In SENDOM the deposition reaction is kinetically favored on the -CH_3 terminated SAMs but transport of reactants is preferred on the hydrophilic -OH terminated SAM. Thus at short deposition times a nanowire forms at the junction of the -OH and -CH_3 terminated surfaces.

9:40am **AP+AS+EM+HI+PS+SS+TF-TuM-6 Anatase Crystalline Phase Discovery on Ultra-Thin Layer TiO2Films During Low-Temperature Ald on Fluorine-Rich Carbon Substrates***, **Brian Butkus**, S. Dabas, C. Feit, J. Ganesan, Z. Parsons, X. Feng, P. Banerjee,* University of Central Florida

A novel approach to crystalline anatase phase in atomic layer deposition (ALD) of $TiO_2$by deposited on a fluorine-rich carbon substrate using titanium (IV) isopropoxide (TTIP) and O_2 plasma. In films deposited at temperatures as low as 100 °C and with a thickness of only 4 nm, highly crystalline anatase phases have been observed. Furthermore, when deposited on glass or silicon substrates other than carbon, TiO_2 films consistently produce amorphous films under these conditions. This talk will highlight the unique substrate-driven crystallization of ALD TiO2 and lays the ground rules for selective crystallization using surfaces with suitable initiation chemistries.

An ALD process using a Veeco® Fiji Gen2 ALD system was used to deposit TiO_2 on hydrophobic, polytetrafluoroethylene-coated carbon substrates (AvCarb GDS2230 from Fuel Cell Store). Temperatures of the ALD ranged from 100 °C to 200 °C, and O_2 plasma (300 watts) and water were used as oxidants. Target film thickness ranged from 4 nm to 22 nm. To characterize the films, Raman, Fourier transform infrared spectroscopy (FTIR), and x-ray photoelectron spectroscopy (XPS) were used. AvCarb GDS2230 substrates with an O_2 plasma as an oxidant resulted in anatase TiO_2 films irrespective of thickness, even when deposited at temperatures below 100 °C. However, the anatase phase is significantly weaker when H_2O is used as the oxidant. An interfacial layer of ALD Al_2O_3 suppresses the growth of the anatase phase. Data from XPS indicates that Ti-F bonds form at the pre-deposition stages of films with anatase TiO_2. On non-fluorinated substrates, where the Ti-F bond does not exist, this structurally distinguishes amorphous TiO_2. This fluorine on the surface of the carbon paper serves as a directing agent[1-5] for the application of TTIP to PTFE in a flourolysis reaction, which drives the TiO_2 to crystallize into anatase films.

Fluorine doped crystallization in Ti-O systems has been reported in sol-gel and hydrothermal approaches to synthesize TiO_2 powders.[6, 7]Here, we report the first gas-phase analog of the above reaction mechanism to synthesize crystalline anatase TiO_2 films. With this strategy, surface initiation chemistries can be used to achieve area-selective and in situcrystallization of films.

11:00am **AP+AS+EM+HI+PS+SS+TF-TuM-10 Site-selective Atomic Layer Deposition: Targeting Electronic Defects***, **Alex Martinson**,* Argonne National Laboratory **INVITED**

While ALD is most commonly employed in uniform conformal growth, more selective precursors and processes may allow for more precise synthetic strategies including targeted reaction at subtly unique surface sites including those that lead to electronic defects. We apply a selective hydration strategy to target reaction at the step edges and/or oxygen vacancies of rutile TiO2 and In_2O_3. We computationally and experimentally investigate the feasibility of facet- and site-selective ALD through accurate asymmetric slab models from which the free energy of adsorption at unique surface sites is leveraged to predict step selectivity. Computational evaluation of ALD precursor adsorption free energies on multiple dehydrated facets further refine the feasibility of a temperature-dependent selective hydration strategy. Initial experiments of Al2O3 and Ga_2O_3ALD nucleation on TiO_2single crystals and MgO ALD on In_2O_3broadly support the computational predictions and strategy. The strategies outlined here provide one possible route to selectively target growth at structural defects of oxide surface that may also act as surface or interface electronic defects.

11:40am **AP+AS+EM+HI+PS+SS+TF-TuM-12 Low Temperature Area-selective ALD and ALE of Pd***, H. Nallan, X. Yang, B. Coffey, **John Ekerdt**,* University of Texas at Austin **INVITED**

Thin film deposition and etching approaches may be constrained by the temperature limits for flexible substrates in roll-to-roll processes.We describe a low temperature ALD route to Pd metal film growth at 100 °C that uses $Pd(hfac)_2$ and H_2.The Pd ALD reaction proceeds in the presence of atomic hydrogen; Pd growth nucleates without delay on a Ni metal seed layer that catalyzes H_2 dissociation.Once nucleated, the evolving Pd surface catalyzes H_2 dissociation.To generate the Ni seed layer, a NiO film is first deposited and reduced with an atomic hydrogen source. The 100 °C ALD of NiO using bis(N,N'-di-*tert*-butylacetamidinato)nickel(II) and H_2O as coreactants is highly selective on exposed oxide surfaces and blocked on organic surfaces.NiO films as thin as 0.5 nm, once reduced to Ni^0, effectively seed Pd growth through catalytic area activation.NiO reduction employs an e-beam heated tungsten capillary at 2.5×10^{-6} Torr H_2 that generates atomic hydrogen to reduce NiO films at 100 °C.

In the event non-selective nucleation occurs on passivated regions, we describe a low temperature ALE route to etch clusters/islands on the passivated regions faster than the desired film.This low temperature route exploits the general findings that metal oxides can be etched by a variety of vapor phase etchants, such as formic acid – the issue is controlled oxidation while minimizing damage to adjacent surfaces.We present a low temperature route that involves VUV ($115 \text{ nm} < \lambda < 180 \text{ nm}$) activation of O_2 to produce atomic oxygen and ozone, with atomic oxygen being the dominant species that oxidizes the near surface region of Pd at 100 °C.Oxidation extents differ between continuous films and discontinuous films enabling the removal of metal islands without significantly etching the film.Density functional theory is used to study the adsorption of oxidants (O and O_3) and describe O diffusion into the films to understand the kinetic limitations of the oxidation step.

Applied Surface Science Division
Room 320 - Session AS+LS+RE+SS-TuM

Synchrotron-Based Photoelectron Spectroscopy Studies of Technologically Important Materials: in Memory of David Shirley

Moderators: James G. Tobin, University of Wisconsin-Oshkosh, **Eric L. Shirley**, National Institute of Standard and Technology

8:20am **AS+LS+RE+SS-TuM-2 Limitations in the Structural Determination of a Close-Packed Overlayer***, **JG Tobin**,* U. Wisconsin-Oshkosh

The close-packed metal overlayer system c(10x2)Ag/Cu(001) has been the subject of extensive electronic structure studies. These include the examination of the two dimensional behavior at low coverages, the development from two- to three-dimensionality and the convergence to three-dimensional dispersion as in Ag(111). It would be of use to have a firmer picture of the placement of the first monolayer Ag atoms ($d_\perp$) versus the Cu(001) substrate. However, it will be demonstrated with FEFF that there are fundamental limitations to the extraction of that information with photon-induced electron diffraction. [1,2]

1. Part of the JVSTA Commemorative Volume of the Career of David A. Shirley

2**.** J. G. Tobin, "Limitations in the Structural Determination of a Close-Packed Overlayer,"J. Vac. Sci. Tech. A **39**, 063203 (2021), https://doi.org/10.1116/6.0001320.

8:40am **AS+LS+RE+SS-TuM-3 Sub-Micron Chemical Speciation Mapping of Uranium Dioxide Aged Under Humid Conditions***, **David Shuh**, A. Ditter, J. Pacold,* Lawrence Berkeley National Laboratory (LBNL)*; Z. Dai, L. Davison,* Lawrence Livermore National Laboratory*; D. Vine,* Lawrence Berkeley National Laboratory (LBNL)*; S. Donald, B. Chung,* Lawrence Livermore National Laboratory **INVITED**

The oxidation of uranium is a critically important process across a variety of fields. It is a key component to understanding the nuclear fuel cycle, the fate and transport of uranium in the environment, and important signatures for nuclear forensics investigations. At room temperature, the humidity of the environment is more important to oxidation than the oxygen content of the atmosphere, so understanding the uranium oxidation can offer important insights into the provenance of a specimen. The scanning transmission X-ray microscope (STXM) at Advanced Light Source (ALS) Beamline 11.0.2 is an instrument capable of chemical speciation mapping below the micron scale. Uranium oxide powder was allowed to age and agglomerate at 98% relative humidity for 378 days, then a focused ion beam (FIB) was used to section a thin slice of this agglomeration for study at the ALS STXM. Results at the oxygen K-edge and uranium N_5-edge identify a bulk, UO_2 phase and an interfacial, schoepite phase, located in distinct regions of the sample. A modified non-negative matrix factorization (NMF) method was used to separate out the primary spectral components and identify these two phases, along with a surface phase which is suspected to be water adsorbed to the surface of the sample. Use of the STXM to identify uranium phases, particularly when coupled with FIB sectioning and NMF analysis is a promising method for uranium analysis going forward.

9:20am **AS+LS+RE+SS-TuM-5 On Photoelectron Spectroscopy and the Shirley Background***, **Eric L. Shirley**,* NIST **INVITED**

Photoelectron spectroscopy and allied spectroscopies, electron-yield and Auger, provide rich information about occupied and unoccupied electron states in solids. Photoelectron spectroscopy and momentum-resolved photoemission allow one to probe band structure. However, photoemission is also plagued by inelastic losses, which occur because creation of additional excitations in the sample lowers a photoelectron's kinetic energy, usually manifested in the form of "satellite peaks." This can be a nuisance in some cases, because complicated interpretation is required when analyzing photoelectron spectra, but it also affords insight into the additional excitations. Background subtraction, such as is done using, say the "Shirley background," is one method used distill spectral features. Measuring electron-yield versus photon energy can be an excellent method for obtaining x-ray absorption spectra, and this can be accomplished using the same electron analyzers as for photoemission. Auger spectroscopy is also feasible using such analyzers, and the small angular acceptance of many current analyzers at hard-x-ray photoelectron spectroscopy (HAXPES) beamlines provides Auger spectroscopy with additional insight into unoccupied states, as will be shown. In this talk, we will survey theoretical treatments applied in connection with many of the above spectroscopies, discussing both insights gained and the treatments' limitations.

11:00am **AS+LS+RE+SS-TuM-10 Origin of the Complex Main and Satellite Features in Oxides***, **Paul S. Bagus**,* University of North Texas*; C. Nelin, C. Brundle, B. Crist,* Consultant*; N. Lahiri, K. Rosso,* PNNL **INVITED**

The assignment of the complex XPS features of the cations in ionic compounds has been the subject of extensive theoretical work. However, there are strong disagreements, even for the origin of the main peaks, [1-2] and the agreement with experimental observations remains insufficient for unambiguous interpretation. In particular, previous cluster model treatments were not able to properly describe the satellite features for the cation XPS. Here we present a rigorous *ab inito* treatment of the main and satellite features in the cation 2p XPS of Fe_2O_3 and NiO which resolves this problem and provides a comparable treatment of both main and satellite features. This has been possible based on a new method for the selection of orbitals that are used to form the ionic wavefunctions. This method is a state averaging of the optimized orbitals over a mixture of normal and shake configurations. The normal configurations have only an electron removed from the cation 2p shell and the shake configurations include, in addition, an electron moved from orbitals of dominantly O(2p) character into the partly filled orbitals of dominantly cation 3d character. Previous cluster model XPS studies had used orbitals optimized only for the normal configuration. [1-2] Thus, for the first time, it is possible to have a set of orbitals that can describe, with comparable accuracy, both the normal and shake configurations. [3] This is especially important since, both in the states for the main and for the satellite XPS features, the normal and shake configurations can, and often do, mix. Thus, comparable accuracy is necessary to have proper descriptions of the ionic final states. It is also important that the character of the ionic states in terms of the occupations of the open shell core and valence orbitals and of the contributions of $2p_{1/2}$ and $2p_{3/2}$ ionization to the XPS intensities have been also determined. Thus, we are able to resolve the ongoing disagreement for the assignment of some regions of the spectra to normal configurations and other regions to shake, or charge transfer, configurations. This is possible because the theoretical treatment, based on cluster models of the oxides, allows us to obtain a detailed level of information about the character of the ionic configurations.

1. P. S. Bagus, E. S. Ilton, and C. J. Nelin, Surf. Sci. Rep. **68**, 273 (2013).

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Biomaterial Interfaces Division
Room 318 - Session BI1+AS+EM+NS+SE+TF-TuM

Bioanalytics, Biosensors and Diagnostics

Moderators: Caitlin Howell, University of Maine, **Laura Mears**, TU Wien, Austria

8:00am **BI1+AS+EM+NS+SE+TF-TuM-1 Understanding and Employing Adhesion Forces in Microfluidic Channels for Cell Separation***, **Avi Gupta**, F. Chrit, A. Liu, A. Alexeev, T. Sulchek,* Georgia Institute of Technology, USA

Rapid advancements in microfluidic technologies during the past few decades have significantly aided advancements in the field of BioMEMS. These technologies can facilitate development of easily scalable tools that can be translated to point-of-care healthcare products. Researchers have capitalized on these tools to create differential separation techniques that rely on adhesion forces. The adhesive interactions play a significant role in governing the trajectory of cells in microfluidic channels as well as the reliability of these devices, however, a concise model explaining cell interactions with chemically coated surfaces is yet to be developed. This research describes studies using microfluidic flow at different flow regimes to study dynamic cell adhesion. APTES, P-selectin, and Pluronic were used as models for non-specific adhesion, specific adhesion, and adhesion-free surfaces, respectively. A microfluidic device with slanting ridges was used to provide forced contact and to visualize the effect of these chemistries on cell trajectories using a microscope and a high-speed camera. Parameters of the channel that were studied include ridge angle, gap size, channel width, and flow rate. It was found that adhesive forces modulate the interaction time of cells during contact points with the slanting ridges. At an average flow velocity of 3.1 cm/sec we observed higher interaction time for APTES coatings and lower for Pluronic coatings. Higher adhesion on APTES coated surface of the channel leads to more deflection of cells towards the streamlines leading them to go opposite to the ridge direction. In contrast, lower surface adhesion on Pluronic coated surface made cells deviate along the ridge perpendicular to streamlines. Narrow channel widths and acute ridge angles helped in exaggerating the differences in trajectories of cells going along or under the ridge. Atomic force microscopy (AFM) was used to quantify the adhesion forces. This knowledge was used to develop a predictive model employing Lattice Boltzmann techniques along with Morse potential and Bell model to represent interaction between cells and device surface. This improved understanding of adhesion forces in microfluidic devices opens new avenues for developing separation techniques that don't employ specific molecules like P-selectin but rely upon the inherent geometry and surface interaction of the cells with a microfluidic channel.

8:20am **BI1+AS+EM+NS+SE+TF-TuM-2 Wafer-Scale Metallic Nanotube Arrays with Highly Ordered Periodicity for SERS Application***, **Jinn Chu**,* National Taiwan University of Science and Technology, Taiwan

This paper reports on the wafer-scale fabrication of ultrahigh sensitivity SERS substrates using metallic nanotube arrays (MeNTAs) with highly ordered periodicity. Various metals and alloys have been used to prepare MeNTAs via sputtering over a contact-hole array template created in photoresist. These include ferrous (stainless steel) and nonferrous (Cu-, Ni-, Al-, and Ti-based) alloys, as well as elemental metals (Cu, Ag, and Au). The proposed nanotubes can be fabricated over a wide range of heights and diameters (from a few hundred nm to 10 µm) in a variety of shapes, including tall cylinders and dishes. In addition, over this is deposited a uniform coating of Au nanoparticles to form a high-sensitivity AuNP@MeNTAs 3D-SERS substrate. Systematic micro-Raman spectroscopic analysis reveal that the fabricated array could function as a SERS-active substrate with crystal violet (CV) and folic acid as analytes (a minimum detection limit of 10^{-13} M CV). Enhancement factor of 1.06×10^9 is obtained from our triangular Ag MeNTA. This work is the first to fabricate wafer-scale metallic nanotube arrays with SERS properties, which represents an important step toward realizing the large-scale fabrication of ultrasensitive SERS-active materials.

8:40am **BI1+AS+EM+NS+SE+TF-TuM-3 Customizing Silk Film Surface Properties Using Plasma-Enhanced Chemical Vapor Deposition***, A. Devore, G. Reyes, **Morgan Hawker**,* California State University, Fresno

Silk fibroin (silk) is a naturally-derived polymer with high utility in biomedical contexts, notably in tissue engineering. Silk bulk properties can be tuned to mechanically match a range of biological environments, including soft and hard tissues. As with other naturally-derived polymers, silk constructs degrade via surface-mediated enzymatic hydrolysis into non-toxic amino acid byproducts. Because tissue engineering relies on the underlying scaffold to degrade as the healthy tissue forms, controlling silk scaffold degradation kinetics is essential to maximize silk's utility. Notably, prior work to control silk degradation kinetics relies on either altering silk matrix properties (i.e., manipulating the secondary structure), or through creating silk-containing blends such as copolymers. Although both strategies effectively control degradation, doing so is often at the expense of mechanical properties. Any mechanical mismatch induced through controlling degradation can hinder scaffold function. Developing a strategy to program silk degradation - without altering bulk mechanical properties - is required to enhance their efficacy as biomaterials.

This talk will highlight recent efforts to develop a radio-frequency plasma-enhanced chemical vapor deposition (PECVD) approach with the potential to modulate silk degradation. The long-term objective of this work is to control the rate of surface-mediated enzymatic hydrolysis by customizing silk surface properties. Surface properties are thought to be paramount in controlling silk construct/enzyme interactions, so tuning silk film surface properties using PECVD was a logical first step. Silk films were first dropcasted, and were then subjected to PECVD. Plasma feedgas composition was tuned using two unique precursors: acrylic acid (to produce thin films with polar functional groups on the silk surface), and pentane (to produce thin films with non-polar functional groups on the silk surface). Plasma polymerization using mixed precursor conditions was also explored. Contact angle goniometry was utilized to evaluate the wettability of all plasma-modified and control silk films. Changes in surface chemistry were evaluated using high-resolution x-ray photoelectron spectroscopy. Collectively, findings demonstrated that surface properties depend on both feedgas composition and position of the silk film in the plasma reactor. In sum, PECVD represents a promising approach to customize silk surface properties.

9:00am **BI1+AS+EM+NS+SE+TF-TuM-4 Biopotential Sensing Using Flexible, Reusable Smart Textile-Based Dry Electrodes*, Jitendra Pratap Singh,*** Physics Dept IIT Delhi, India

Biopotential signals are used to assess organ function and make diagnoses. Biopotential electrodes are used to monitor and record biopotentials by acting as an interface between biological tissue and electrical circuits. The accurate detection of physiological signals from the human body is essential for health monitoring, preventive care, and treatments.

Wearable bioelectronics developments applied directly on the epidermal surface provide a promising future biopotential sensing option. Wearable textile electrodes for biopotential sensing are a promising candidate for long-term health monitoring. Wearable health-monitoring devices should be simple to use, stigma-free, and capable of delivering high-quality data. Smart textiles, which incorporate electronic elements directly into the fabric, offer a seamless way to incorporate sensors into garments for a variety of purposes. This work describes different types of flexible and reusable textile-based dry electrodes for biopotential monitoring. This work also describes the direct writing of laser-induced graphene (LIG) on a Kevlar textile for the production of reusable dry electrodes for long-term ECG monitoring. The electrode as-prepared has a high electrical conductivity and skin contact impedance of 100 ± 1 kΩ to 7.9 ± 2.7 kΩ for frequencies ranging from 40 Hz to 1 kHz, which is comparable to conventional Ag/AgCl wet electrodes.

The outcomes demonstrate comparable performance with significantly reduced electrode-skin impedance for clinical-grade devices. Even after several hours of usage, these electrodes do not irritate the skin and are effective without any skin preparation. As a result of their flexibility and a better match to the modulus of the skin, it is anticipated that the suggested dry electrodes will provide comfort for long-term biopotential monitoring. A simple, cost-effective, and scalable fabrication approach enables the fabrication of flexible electrodes of arbitrary shape for long-term biopotential monitoring.

18. Y. Maithani, B. Choudhuri, B. R. Mehta, and J. P. Singh: Self-adhesive, Stretchable, and Dry Silver Nanorods Embedded Polydimethylsiloxane Biopotential Electrodes for Electrocardiography. *Sensors Actuators A Phys.***332**, 113068 (2021).
19. Y. Maithani, B. Choudhuri, B. R. Mehta, and J. P. Singh: Modelling and Analysis of Active Biopotential Signals in Healthcare , Volume 2 A comprehensive review of the fabrication and performance evaluation of dry electrodes for long - term ECG monitoring. *IOP Publ. Ltd 2020***2**(chapter 8), 1 (2020).

9:20am **BI1+AS+EM+NS+SE+TF-TuM-5 Functional Plasma Polymers for Biosensing Applications*, Melanie McGregor,*** University of South Australia **INVITED**

Materials with intricate nanostructures display wetting properties that modern technologies already use to lubricate engines or waterproof clothing. Yet, their full potential in applications for sustainable catalysis, air purification or biosensing cannot be realised until we understand how nano-objects adsorb to surfaces with features of comparable size. Indeed, controlling or even predicting how proteins, antibodies, exosomes, surfactant or nanoparticles stick to nano-engineered surfaces is a challenge because key aspects of the wetting phenomenon remain poorly understood at this scale. In this talk, I will briefly review what we currently know about "nanowetting".[1] I will then introduce the concept of plasma polymerisation as a technique to control both surface chemistry and surface topography. I'll use the example of plasma deposited polyoxazoline (POx) to highlight this technique's attributes, drawbacks and recent progress made in understanding the unique chemistry and reactivity of POx films, using both plasma in-situ and post deposition spectroscopic analysis.[2]Plasma deposited Polyoxazoline thin films share many valuable properties with polyoxazoline prepared via conventional organic chemistry: they are biocompatible, non-cytotoxic and low fouling.[3] What is more, they bind biomolecules covalently, support cell adhesion, and are generated in a solvent free, single step process, which makes them particularly attractive for industrialization. For these reasons, plasma deposited polyoxazoline are used in applied biomedical research, from in vitro stem cell culture to controlling immune responses.[4]

I'll conclude this presentation with tangible outcomes of the translational research projects I've conducted with various industries, where we used nanoengineered plasma polymers, to create materials for cancer diagnosis and growing organoids.[5]

[1]**M. MacGregor** and K. Vasilev. *Advanced Materials Interfaces,4*, 1700381.,2017**;M. MacGregor** et al., *Nanoscale*, 8(8),4635-4642, 2016

[2] **M. Macgregor***et al.*Chemistry of Materials, 29(19)8047-51,* 2017; **M. N. MacGregor**-Ramiasa et al., *J. Mat. Chem. B*, 3, 6327-6337, 2015

[3]**M. N. Ramiasa** et al. *Chem. Commun.*, 51, 4279-4282,2015**;**A. A. Cavallaro, **M. N. Macgregor**-Ramiasa, K. Vasilev, *ACS Appl. Mater. Interfaces8*, 6354, 2016.

[4] R. M. Visalakshan, A. A. Cavallaro, **M. N. MacGregor**, et al. *Adv. Funct. Mat.*, 29, 1807453, 2019**;**

[5]**M. MacGregor***et al. *Biosensors and Bioelectronics,* 171: 112699,2020; K.M. Chan […]**M. MacGregor****Cancers* 13(21), 5544 2021

Biomaterial Interfaces Division
Room 318 - Session BI2+AS-TuM
Characterization of Biological and Biomaterials Surfaces

Moderators: Kenan Fears, U.S. Naval Research Laboratory, **Graham Leggett**, University of Sheffield, UK

11:00am **BI2+AS-TuM-10 Getting to the Surface of Biology*, Lara Gamble,*** University of Washington **INVITED**

A variety of different surfaces (or interfaces) exist in biology. The surface of a biomaterial is the interface between that biomaterial and the biological environment. State-of-the-art instrumentation, experimental protocols, and data analysis methods are needed to obtain detailed information about these surface and interface structures and their compositions. Surface analysis tools such as time-of-flight secondary ion mass spectrometry (ToF-SIMS) can provide images of polymer biomaterials, cells, and tissues with chemical and molecular specificity. These chemically specific images could revolutionize our understanding of biological processes such as the role of changes in tumor metabolism that affect responses to chemotherapy. Since many biomaterials (e.g. porous polymer scaffolds), cells, and tissues are three-dimensional constructs, it is of interest to be able to characterize their chemical composition in 3D. However, it is challenging to characterize these topographically complex materials with surface-sensitive techniques. With the use of gas cluster ion beams (GCIBs) surface analysis tools such as x-ray photoelectron spectroscopy (XPS) and ToF-SIMS can attain very fine z-resolution (<10 nm) in-depth profiles. In this presentation, ToF-SIMS analysis of biologically relevant samples in 2D and 3D will be presented.

11:40am **BI2+AS-TuM-12 3D Investigation of Sr^{2+} Mobility in Bone Marrow by ToF- and Orbi-SIMS***, C. Kern, A. Pauli, R. Jamous, T. El Khassawna,* ***Marcus Rohnke***, Justus Liebig University Giessen, Germany

Next generation biomaterials will be functionalised with drug release systems. In osteoporosis research strontium ions (Sr^{2+}) have emerged as promising therapeutic agent in modified bone cements for better fracture healing. In previous work we focused on the Sr^{2+} release off a functionalised bone cement and its dispersion in the mineralised areas of rat bone. [1, 2] Here, we go one step further and investigate Sr^{2+} transport within the much more complex system bone marrow in a passive dispersion experiment. First, we present an experimental cryo-workflow for transport studies within bovine bone marrow. As analytical tools for tracking the Sr^{2+} diffusion in 3D and spatially resolved characterisation of the bone marrow we apply time-of-flight secondary ion mass spectrometry (ToF-SIMS) and orbitrap secondary ion mass spectrometry (Orbi-SIMS). Within a time-dependent experimental series, the validity of our experimental approach is shown. Average diffusion coefficients of Sr^{2+} in bovine bone marrow in fast diffusion areas ($D_{\mathrm{bovine,FD}}=(2.09\pm2.39)\cdot10^{-9}$ cm^2s^{-1}), slow diffusion areas ($D_{\mathrm{bovine,SD}}=(1.52\pm1.80)\cdot10^{-10}$ cm^2s^{-1}), and total area diffusion ($D_{\mathrm{bovine,TA}}= (1.94\pm2.40)\cdot10^{-9}$ cm^2s^{-1}) were obtained. In a subsequent proof-of-concept study, we successfully applied the developed protocol to the determination of Sr^{2+} diffusion in bone marrow of osteoporotic rats [fast diffusion: $D_{\mathrm{rat,FD}}=(9.02\pm5.63)\cdot10^{-10}$ cm^2s^{-1}); slow diffusion: ($D_{\mathrm{rat,SD}}=(6.48\pm3.88)\cdot10^{-10}$ cm^2s^{-1}); total area diffusion ($D_{\mathrm{rat,TA}}= (8.89\pm5.37)\cdot10^{-10}$ cm^2s^{-1}]. Detailed 2D and 3D mass spectrometric imaging analysis as well as Orbi-SIMS spectral analysis revealed that Sr^{2+} diffusion is slower in bone marrow areas with high intensity of lipid and fatty acid signals than in areas with less intensity of lipid signals. Overall, our results provide important insights about Sr^{2+} diffusion in bone marrow and we are able to show that both cryo-ToF-SIMS and Orbi-SIMS are useful tools for the investigation of rapid diffusion in water-containing highly viscous media.

[1] M. Rohnke, S. Pfitzenreuter, B. Mogwitz, A. Henß, J. Thomas, D. Bieberstein, T. Gemming, S.K. Otto, S. Ray, M. Schumacher, M. Gelinsky, V. Alt, Strontium release from Sr^{2+}-loaded bone cements and dispersion in healthy and osteoporotic rat bone, J. Controlled Release **262** (2017) 159

[2] C. Kern, M. Quade, S. Ray, J. Thomas, M. Schumacher, T. Gemming, M. Gelinsky, V. Alt, M. Rohnke, Investigation of strontium transport and strontium quantification in cortical rat bone by time-of-flight secondary ion mass spectrometry, J. R. Soc. Interface **16** (2019) 20180638

12:00pm **BI2+AS-TuM-13 Comparison of NAP-XPS and Cryo-XPS for Studies of the Surface Chemistry of the Bacterial Cell-Envelope***,* ***Paul Dietrich****,* SPECS Surface Nano Analysis GmbH, Germany*; M. Kjærvik,* BAM Berlin, Germany, Norway*; M. Ramstedt,* Umeå University, Sweden*; W. Unger,* BAM, Germany

Bacterial interactions with the environment are based on processes involving their cell-envelope. Thus, techniques that can analyze their surface chemistry are attractive tools for providing an improved understanding of bacterial interactions. One of these tools is x-ray photoelectron spectroscopy (XPS) with an estimated information depth of <10 nm for Al Kα-excitation. XPS-analyses of bacteria have been performed for several decades on freeze-dried specimens to be compatible with the classical ultra-high vacuum conditions needed. A limitation of these studies has been that the freeze-drying method may collapse cell structure. However, recent developments in XPS allow for analysis of biological samples at near ambient pressure (NAP-XPS) or as frozen hydrated specimens (cryo-XPS) in vacuum. In this talk, we present the analysis of bacterial samples from a reference strain of the Gram-negative bacterium *Pseudomonas fluorescens* using both techniques. We will present the results obtained and, in general, observed good agreement between the two techniques. Furthermore, we will discuss advantages and disadvantages of these two analysis approaches and the output data they provide. XPS reference data from the bacterial strain are provided, and we propose that planktonic cells of this strain (DSM 50090) to be used as a reference material for surface chemical analysis of such bacterial systems.

Chemical Analysis and Imaging Interfaces Focus Topic
Room 302 - Session CA+AS+SE+SS-TuM

Progress and Challenges in Industrial Applications

Moderators: Alex Tselev, University of Aveiro, Portugal, **Xiao-Ying Yu**, Oak Ridge National Laboratory, USA

8:00am **CA+AS+SE+SS-TuM-1 Progress on Commercializing Doped Diamond Materials and Devices***,* ***Anna Zaniewski,*** Advent Diamond **INVITED**

Diamond has long been recognized as a potentially transformative material for power, sensor, and quantum applications. However, realizing the potential of diamond has depended upon a series of breakthroughs in the growth, design, and fabrication of diamond for electronics. Most notably, CVD growth of doped diamond has been a catalyzing breakthrough for realizing next-generation diamond components. Advent Diamond will present progress on achieving commercialization of diamond components and outline future targets for semiconducting and quantum devices.

8:40am **CA+AS+SE+SS-TuM-3 Advanced in Situ Transmission Electron Microscopy: A Powerful Tool for Materials Science, Catalysis, Energy Storage & Lifescience Applications***,* ***Hugo Pérez-Garza,*** DENSsolutions, Netherlands **INVITED**

We introduce our technology for in situ studies inside transmission electron microscope (TEM), where next to heating and biasing studies, also environmental studies (i.e. in gaseous or liquid environments) are made possible. The systems rely on a Micro Electro-Mechanical System (MEMS)-based device as a smart sample carrier, which contains an integrated set of biasing electrodes or an integrated microheater, to enable in situ electrochemistry, catalytic studies, failure analysis and biomedical studies, among others. As a result, the system provides users with the capability to visualize exciting dynamics in vacuum or liquid/gas environments as a function of different stimuli. In order to provide meaningful results and address historical challenges, our MEMS device controls the flow direction and ensures the gas/liquid will always pass through the region of interest. Thereby, the developed systems offer the opportunity to define the mass transport and control the kinetics of the reaction. Furthermore, the systems allow to control the liquid thickness, enabling resolutions that can go even down to 2.15 Å (for a 100nm liquid thickness). We believe that our developments will play a fundamental role in addressing many of the research questions within battery optimization, fuel cells, (electro)catalysis, as well as for advanced (bio)materials and nanomedicine. Furthermore, it will the unique possibility to visualize biological processes in real time, without the need of vitrifying the biological specimen.

Keywords: Transmission electron microscopy, in situ, MEMS, environmental studies, stimuli

9:20am **CA+AS+SE+SS-TuM-5 Chemical Analysis Using Laboratory-Based Hard X-Ray Photoelectron Spectroscopy: The Binding Energy Reference Challenge***, A. Vanleenhove, F. Mascarenhas,* ***Thierry Conard,*** IMEC, Belgium

XPS is a well-established technique used for non-destructive analysis of the chemical composition of thin layers and interfaces and is most commonly performed using Al Kα radiation (1486.6 eV), which limits the analysis to the top 5-10nm. The recently developed laboratory-based hard X-ray photoelectron spectroscopes (HAXPES) provide new analysis options. They enable the analysis of thicker film structures and interfaces buried down to 20-50 nm depending on the photon energy and facilitate the analysis of fragile buried layers without ion-induced chemical damage.

This new in-lab technology however comes with new challenges. By the increase of effects which were less pronounced or did not play a role in the analysis with soft X-ray photoelectron spectroscopy the exact binding energy determination and hence analysis of chemical bonding inside layers and at interfaces is more challenging. The recoil effect for instance, which is related to preservation of momentum, resulted in electron energy shifts well within the error bar of peak position determination for XPS spectra. For HAXPES, the recoil effect has to be taken into account, especially when examining low Z materials. Charging effects play a bigger role as well. While charging has to be taken into account for XPS, the analysis of most XPS spectra is quite straightforward as long as the surface charge is stable and the lateral distribution of surface charge is uniform within the area of analysis. For HAXPES however vertical charge distribution comes into the game for a large group of structures whose development can benefit from

HAXPES analysis. Vertical charge build up can be complex, especially if examined structures exist of multiple layers and hence multiple interfaces, containing a large variety of materials. But even in ‘simple’ non-conducting one-layer structures a vertical charge gradient builds up when exposed to X-rays and small changes in the parameters of standard surface charge neutralization techniques - as the use of e-beam flood guns - can influence the nature of the charge gradient.

HAXPES spectra of technologically relevant samples will be discussed to demonstrate the challenge of determining exact binding energy values. The set of examined samples comprises complex oxide layers with varying thickness on Si samples and metal/high-k/Si stacks including high-k materials as HfO_2. All experiments are performed in a PHI *Quantes* system and/or a Scienta Omicron *HAXPES Lab*, both equipped with two monochromatic X-ray sources: an Al Kα (1486.6 eV) and a Cr Kα (5414.8 eV - *Quantes*) or Ga Kα (9252.1 eV – *HAXPES lab*) X-ray source.

Acknowledgement

We are grateful to the Research Foundation Flanders (FWO) for funding the *HAXPES Lab* instrument within the HERCULES program for Large Research Infrastructure of the Flemish government. Project I014018N.

11:00am **CA+AS+SE+SS-TuM-10 Integrating Spatial Multiomics Using Giant Cluster Imaging Mass Spectrometry at the Single-Cell Level*, Hua Tian,*** University of Pittsburgh **INVITED**

Tissue is highly organized with diverse cells that interact and communicate. Together with numerous biomolecules (e.g. metabolites and lipids) of cellular processes, the multilevel heterogeneities drive the biological function and disease-associated discoordination$^{1-2}$. This spatial complexity is often ignored by traditional tissue assay. Mass spectrometry imaging holds the potential to visualize the heterogeneous cell organization and biomolecules in their context. However, it is challenging to achieve high spatial resolution and high chemical sensitivity toward different biomolecules. Moreover, the correlation of spatial omics in a single sample is impossible due to the difficulty of preserving the fast-changing metabolites.

To overcome these analytical hurdles, innovative technology and methodology are developed for omics imaging in single cells. On the same frozen-hydrated tissue, successive $(H_2O)_{n\ (n>28k)}$-GCIB-SIMS and C_{60}-SIMS imaging are employed to profile untargeted metabolites/lipids and targeted proteins by lanthanides antibodies (~ 40 in one acquisition) at 1 µm resolution. The novel ion source, $(H_2O)_{n(n>28k)}$-GCIB enhances chemical sensitivity, improves beam focus, reduces matrix effect, and extends detection ranges up to m/z 6000 $^{3-12}$. Coupled with cryogenic analysis, the tissue is analyzed at near nature state, retaining the spatiotemporal distribution of metabolites and lipids. The AI-aided computational processing is used to register the omics in different cell types for further discriminant analysis.

With the new development, a number of tissues are imaged. On breast cancer tissue, the high population of macrophages (CD68) and less infiltration of immune cells (CD45, CD4) are observed, as well as the variation of the metabolic state in different cells. Several phosphatidylinositol species are concentrated in the epithelial tumor cells (pan-cytokeratin), along with desaturated lipids and GSH, indicating the mechanism of immune resistance and antioxidation for tumor survival ^{27}. Eight ganglioside GM3s correlate with the Ki-67 expressing cells, likely the markers of neoplastic transformation of breast tissue^{37}. On liver tissue, distinct lipid clusters colocalize with periportal and pericentral proteins, and metabolic and lipidomic signature varies in distinct liver cells (*e.g.,* sinusoidal, Kupffer, hepatocytes, Ito stellate, immune cells). Similar to protein markers, further clustering analysis shows that metabolites and lipids classify the cell types for the first time. The multimodal SIMS imaging opens broad applications for exploring various biological phenomena of cellular/biomolecular interactions in health/disease.

11:40am **CA+AS+SE+SS-TuM-12 Atom Probe Tomography Using Wavelength-Tunable, Femtosecond-Pulsed Coherent Extreme Ultraviolet Radiation*, Ann Chiaramonti,*** *B. Caplins, J. Garcia, L. Miaja-Avila, N. Sanford,* National Institute of Standards and Technology (NIST) **INVITED**

Laser-pulsed atom probe tomography (LAPT) is a powerful tool for materials characterization due to its desirable combination of high spatial resolution and analytical sensitivity. In state-of-the-art LAPT, the thermal pulse resulting from a near-ultraviolet (NUV) laser (E=3.5 eV to 3.6 eV; λ=355 nm to 343 nm) incident on the sample provides the energy to overcome the activation barrier for field ion evaporation.LAPT has been used successfully to characterize a wide range of materials including metals, semiconductors, insulators, biological materials, and even liquids. However, the thermal process is not without drawbacks. LAPT data quality can be degraded due to for example: thermal tails that limit sensitivity; the formation of cluster ions that may have isobaric overlap with elemental species; undetected neutral species which can adversely influence composition measurements; and unresolvable multiple hits which result in a loss of information. Data loss due to multiple hits and neutral species is particularly problematic for many ionic and covalent materials; it can limit the recovery of bulk stoichiometry or composition to a narrow range of experimental conditions, if at all [1,2].

Ionizing radiation in the extreme ultraviolet (EUV) region of the electromagnetic spectrum (E=10 eV to 100 eV; λ=124 nm to 12 nm) offers potential new field ionization pathways (e.g. direct photoionization and Auger decay) for atom probe tomography.Much of the EUV photon energy band is above the work function and ionization potential of any naturally occurring element, and photoionization cross-sections peak in the EUV band across the entire periodic table [3]. EUV is also highly absorbed within only the first few nm of the sample surface.

Instrument design and results from the world’s first EUV radiation-pulsed atom probe microscope are presented. This instrument uses tunable wavelength (photon energy) femtosecond-pulsed coherent EUV radiation from phase-matched high harmonic generation in a hollow waveguide. Initial experiments demonstrate successful EUV (E=41.85 eV; λ=29.6 nm) radiation-pulsed field ion emission in a variety of materials systems. Time-independent background levels, delayed evaporation tails, peak widths, charge state ratios, multiple hit counts, and the relative number of cluster ions will be compared to NUV LAPT experiments on the same samples and specimens.

[1] Mancini, L. *et al*. J. *Phys. Chem. C***118** (2014) 24136.

[2] Diercks, D.R. *et al. J. Appl. Phys.***114** (2013) 184903.

[3] Yeh, J.-J. and I. Landau. *At. Data Nucl. Data Tables***32** (1985) 1.

Spectroscopic Ellipsometry Focus Topic
Room 304 - Session EL+AS+EM-TuM

Optical Characterization of Thin Films and Nanostructures

Moderators: Tino Hofmann, University of North Carolina at Charlotte, **Mathias Schubert**, University of Nebraska - Lincoln

8:00am **EL+AS+EM-TuM-1 Femtosecond Time Resolved Pump-Probe Spectroscopic Ellipsometry – Applications and Challenges*, Rüdiger Schmidt-Grund,*** TU Ilmenau, Germany **INVITED**

I will introduce the method fs-time resolved pump-probe spectroscopic ellipsometry (TSE), recently developed by us [1], as a mighty instrument to investigate the electronic structure and lattice properties of materials in great detail, going beyond many established experimental methods. TSE measures the transient complex dielectric function after optical excitation of charge carriers, which gives us a powerful tool to probe band structure, joint-density of states and transition matrix elements in various regions of the Brillouin zone as well as dynamic phenomena like carrier-carrier scattering, carrier-phonon scattering, excitation, and relaxation. As all this properties and effects in general also depend on the transient carrier density, analysis of TSE data provides vast knowledge about the electronic structure dynamics of materials, in particular valuable for fundamental theory approaches.

After excitation with an intense pump-laser, electrons and holes are created in the conduction and valence bands, respectively. These excited carriers then can scatter within the Brillion zone and interact with the lattice. This leads to dynamic carrier distribution changes in energy and momentum within time scales of fs up to ns or longer. The ellipsometry probe pulse then feels the actual energetic charge carrier distribution at a given delay time step, as expressed in changes of the dielectric function due to Pauli blocking or enabling of new transitions, energy shifts, as well as Drude response induced by these excess carriers in the respective band states. When modelling the experimentally found transient dielectric function with appropriate line shape model functions under mutual comparison with theoretically obtained data for the band structure and joint density of states, we can identify the positions of the charge carriers within the band structure in time, energy, and momentum.

Modelling TSE data is a very complex task: The spatial distribution of the excited carriers must be considered in transfer-matrix analysis, many time-delay steps have to be analysed simultaneously in model function approximation to identify positive and negative contributions as well as to obtain physically meaningful time-evolution of the parameters, and many more challenges. To circumvent the problems, we apply machine-learning based algorithm to find the best modelling of the data.

In my presentation I will introduce technical details of the method TSE, discuss modelling strategies, and give examples of processes observed in various material systems.

[1] S. Richter, M. Rebarz, O. Herrfurth, S. Espinoza, R. Schmidt-Grund, and J. Andreasson, Rev. Sci. Instrum. 92, 033104 (2021)

8:40am **EL+AS+EM-TuM-3 Evolution of Anisotropy and Order of Band-to-Band Transitions, Excitons, Phonons, Static and High Frequency Dielectric Constants Including Strain Dependencies in Alpha and Beta Phase ($Al_XGa_{1-X})_2O_3$,** ***Megan Stokey****, R. Korlacki, M. Hilfiker, T. Gramer, J. Knudtson,* University of Nebraska-Lincoln*; S. Richter,* Lund University, Sweden*; S. Knight,* Linkoping University, Sweden*; A. Mock,* Weber State University*; A. Mauze, Y. Zhang, J. Speck,* University of California Santa Barbara*; R. Jinno, Y. Cho, H. Xing, D. Jena,* Cornell University*; E. Ahmadi,* University of Michigan*; V. Darakchieva,* Lund University, Sweden*; M. Schubert,* University of Nebraska-Lincoln

The rhombohedral alpha and monoclinic beta phases of gallium oxide both make promising candidates for ultra-wide bandgap semiconductor technology. Of particular interest are alloyed films and the evolution of anisotropic optical properties with respect to both alloy composition and strain induced effects. Here, we study alpha and beta phase $(Al_xGa_{1-x})_2O_3$ via a combined density functional theory and generalized spectroscopic ellipsometry approach across a range of alloying. Infrared-active phonon properties, static dielectric constants and midband gap indices of refraction are quantified.[1,2,3] Strain and alloying effects are shown and compared to previous theoretical works.[4] Bandgaps, excitons, and high-frequency dielectric constants are also investigated in the visible to vacuum-ultra-violet (VUV) spectral range.[5,6,7,8] We identify a switch in band order where the lowest band-to-band transition occurs with polarization along the ordinary plane in α-$Ga-_{-2}O-_3$ whereas for α-$Al-_2O_3$ the lowest transition occurs with polarization in the extraordinary direction. With this, we present the most comprehensive picture of optical properties' evolution along composition and strain currently available.

[1] M. Stokey, R. Korlacki, *et al.,* Phys. Rev. Materials 6, 014601 (2022)

[2] M. Stokey, T. Gramer, *et al.,* Appl. Phys. Lett. 120, 112202 (2022)

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9:00am **EL+AS+EM-TuM-4 Engineering the Bi-Signate Broadband Enhanced Chirality Revealed by All Dielectric *Nanoboomerang* Structure*,* *Ufuk Kilic**, *M. Hilfiker, A. Ruder, S. Wimer, S. G. Kilic, E. Schubert, C. Argyropoulos, M. Schubert,* University of Nebraska-Lincoln

Chirality phenomenon has recently aroused remarkable interest because of its promising potential applications in optics, catalysis and sensing. However, the large-scale mismatch between the wavelength of incident circular polarized (chiral) light and the size of natural chiral crystals (such as quartz or benzyl) or small size of chiral molecules (such as DNA or proteins) led the chiral light-matter interactions to be extremely weak in nature and cannot be made tunable [1]. The recent studies showed that one can obtain strong and tunable chiral response using subwavelength scale structures so-called metamaterials. As a promising large-scale area, bottom-up 3D nanomorphology fabrication method with precise sample stage manipulation ability, the glancing angle deposition (GLAD), is envisioned as a promising route to the experimental realization of strong and tunable chiroptical responses [1].

Here, we propose a simplistic chiral-nano-platform: all-dielectric spatially coherent, superlattice type, distorted L-shape metamaterials so-called chiral *nanoboomerangs* which were fabricated using custom-built, ultra-high-vacuum electron beam evaporated GLAD instrument. The structure consists of two achiral silicon nano-columnar segments, but the sample stage is rotated prior to the fabrication of second segment. Using a Mueller matrix spectroscopic ellipsometry based chiroptical characterization method, we found that our proposed large-scale nanophotonic metamaterial platform exhibits extremely broadband, large, tunable, and bi-signate chiroptical response within the near infrared to vacuum ultraviolet spectral range. We believe that this new material platform is a strong candidate for a myriad of next generation photonic integrated technological applications including but not limited to chiral sensors, drug-delivery systems, and chiral-topological insulators.

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9:20am **EL+AS+EM-TuM-5 Structural Properties and Optical Constants of CaF_2 at 300 K from 0.03 to 6.5 eV*,* *Jaden R. Love**, *N. Samarasingha, C. Armenta, S. Zollner,* New Mexico State University*; H. Kim,* National Institute of Aerospace (NIA)

In this undergraduate student presentation, we describe the structural and optical properties of calcium fluoride (CaF_2) an insulator with an ultrawide band gap of 12 eV and a large exciton binding energy of 1 eV. CaF_2 has a wide range of transparency from 125 meV in the infrared to 10 eV in the ultraviolet making it an ideal substrate for optical devices. Such optical devices include actively tunable transmission filters utilizing certain phase change memory materials (PCM's) which can be used for higher resolution imaging on satellites. Most studies of the optical constants of CaF_2 were performed in the 1960's and are discussed in [1]. Revisiting these optical constants using modern ellipsometry equipment and specimens from different manufacturers with (100) and (111) orientation seems timely. CaF_2 crystallizes in the fluorite structure with space group Fm-3m and has a lattice constant of 5.4626 Å. The $Ca-^{2+}$ atoms are located in the Wyckoff (4a) position at the origin. The F^- atoms are at the (8c) positions (¼,¼,¼) and (¼,¼,3/4). There is a three-fold degenerate Raman-active T_{2g} mode and a three-fold degenerate infrared active T_{2u} mode, which splits into a transverse optical (TO) doublet and a longitudinal optical (LO) singlet. The T_{2u} mode can be observed with Fourier-transform infrared ellipsometry and described with a Lorentzian. The TO and LO energies are 261 and 477 cm^{1-}, respectively, with an amplitude A=4.1, a broadening of 4 cm^{1-}, and a high-frequency dielectric constant of 1.98[1]. A dip in the reststrahlen band is due to two-phonon absorption described with an anharmonically broadened Lorentzian. In the visible and near ultraviolet approaching 6.5 eV, normal dispersion can be described with a pole located at 7.48 eV and a Tauc-Lorentz oscillator at 20 eV. The imaginary part of the pseudo dielectric function, $<\varepsilon_2>$ is negative above 3 eV. This indicates a surface layer of 2 to 5 nm thickness with a larger refractive index than that of the bulk substrate. We apply the CaF_2 optical constants to determine the thickness of an SiO_2layer on the CaF_2 substrate.

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9:40am **EL+AS+EM-TuM-6 Optical Dielectric Function of a Solution-Processable Thiazolothiazole Thin Films Determined by Spectroscopic Ellipsometry*,* *Nuren Shuchi**, *J. Mower, V. Stinson, M. McLamb, G. Boreman, M. Walter, T. Hofmann,* University of North Carolina at Charlotte

Fluorescent molecules are ubiquitous in contemporary technologies and can be found for instance in energy-conversion devices [1], sensors [2], and are used for biological imaging techniques [3]. Recently, families of fluorescent molecules which combine multiple functionalities have gained considerable attention [4]. Significant progress has been made in the field of molecular electronics due to the advent of unique oligothiophenes [5] and thiadiazolobithienyl dyes [6]. We have synthesized solution-processable, 2,5-bis(N,N-dibutyl-4-aminophenyl)thiazolo[5,4-d]thiazole (TTz) dyes for thin film organic electronics applications. The TTz dyes were synthesized by refluxing 4-pyridinecarboxaldehyde, 4-(dibutylamino)benzaldehyde, and dithiooxamide in 40 mL of anhydrous dimethylformamide for 6 hours at 120 °C. The reaction solution was chilled overnight and crude precipitate was collected using vacuum filtration and rinsed with dimethyl sulfoxide and water. The isolated product was purified using silica gel column chromatography (Silica Flash M60) with a 1:1 hexanes/chloroform mixture. <1,0,0> Si wafers were cut to approximately 20 mm x 15 mm and sonicated in acetone, deionized water, and isopropyl alcohol for 15 minutes. The wafers were dried with compressed nitrogen gas and treated with UV / ozone for 15 minutes. The Si wafers and a 16.1 g/L 1,2-dichlorobenzene solution of the thiazolothiazole dye were heated to 55 °C in a nitrogen glove box. While in the glove box, 90 µL of the TTz solution was spin coated onto each Si wafer at 2000 RPM for 30 seconds. The wafers were heated to 110 °C for 20 minutes and stored in the glove box away from light. In this presentation, we will discuss spectroscopic ellipsometry data obtained from a 2,5-bis(N,N-dibutyl-4-aminophenyl)thiazolo[5,4-d]thiazole thin films deposited by spin coating on a silicon substrate in the spectral range from 354 nm to 1907 nm. The ellipsometric data were analyzed using a stratified layer model composed of thiazolothiazole thin film, native SiO_2 oxide, and Si substrate. The model dielectric function of the thiazolothiazole thin film was composed of a series of Tauc-Lorentz and Gaussian oscillators. The best-model calculated data are rendering the experimental data very well. Obtained transition energies will be reported and compared with those of related thiazolothiazole dyes. **References:** [1] J. Am. Chem. Soc. **133**, 20009 (2011). [2] Chem. Soc. Rev. **40**, 2222 (2011). [3] BMC Systems Biology **2**, 1(2008). [4] CHEM-EUR J. **19**, 2582 (2013). [5] J. Phys. Chem. Lett. **9**, 1958 (2018). [6] Sci. Rep. 6, 18870 (2016).

11:00am **EL+AS+EM-TuM-10 Bandgap Engineering of Polycrystalline Ge-doped Sb_2Se_3 Thin-Film: Surface and Optical Properties***, **Sanghyun (Philip) Lee**,* University of Kentucky*; M. McInenery,* Rose-Hulman Institute of Technology

Antimony Chalcogenide, $Sb_2(S_x,Se_{1-x})_3$ is a third-generation thin-film photovoltaic device. $Sb_2(S_x,Se_{1-x})_3$ solar cells have received growing attention due to their favored properties with <9.2 % efficiency. In particular, $Sb_2(S,Se)_3$ has a high absorption coefficient at visible light (>10^5 cm^{-1}), tunable bandgap (1.0 eV – 1.7 eV), stable upon exposure to sunlight under ambient conditions.

For the optimization of bandgap of Sb_2Se_3 alloy films, Ge-doped Sb_2Se_3 thin-film for solar cells applications have been studied with various compositions and doping concentrations, showing different crystallization, surface, and optical characteristics. Sb_2Se_3 thin-films are crystalline as deposited and on heating with orthorhombic structures. As a few molar percent of Ge doped into Sb_2Se_3 (<15 %) films (GeSbSe), polycrystalline films are formed upon annealing above 200 - 250 C, demonstrating no significant dependence of lattice constant on the Ge doping level. However, most GeSbSe studies are focused on amorphous Sb_2Se_3 films doped with higher Ge concentration (> 15 %).

In this contribution, we have fabricated and studied the bandgap energy and surface properties of polycrystalline GeSbSe thin-films (<15 %) for the application to the photovoltaic absorber. We investigated critical optical properties of absorption coefficient and engineered optical bandgap of films grown at different temperatures. Optical responses are explored with UV-Vis spectrometer. Moreover, scanning electron microscopy and Energy-dispersive X-ray spectroscopy are used to confirm optical bandgap, surface structures, and chemical composition of GeSbSe thin-films grown by Vapor Transport Deposition at different film growth temperatures. The optimum optical characteristics of thin-film absorber materials depend on film surface microstructure, which in turn affects the overall optical behaviors of GeSbSe films.

Ge-doped Sb_2Se_3 thin-films (<15 %) are polycrystalline with thickness around 1 um grown at 500 C and 520 C. As the deposition temperature increases from 500 C to 520 C, uniform grains of approximately 0.9 um at 500 C become mixed grains of larger (~6 um) and smaller grains (~0.9 um), revealed by Scanning Electron Microscopy characterization. The surface morphology becomes smooth (500 C) to irregularly rougher (520 C). For the characterization of optical properties, the absorption coefficient is >10^5/cm near 600 nm for both films. Based on the widely used Tauc's relation, the optical bandgap of Ge-doped Sb_2Se_3 thin-film absorbers is extracted as 1.15 eV and 1.23 eV for samples grown at 500 C and 520 C, respectively.

11:20am **EL+AS+EM-TuM-11 Optical Properties of Orthorhombic $LiGa0_2$ from Far-Infrared to Vacuum Ultraviolet***, **Teresa Gramer**, E. Williams, M. Stokey, R. Korlacki, U. Kilic, M. Hilfiker, M. Schubert,* University of Nebraska - Lincoln

Within the Li_2O-Ga_2O_3 oxide system, $LiGaO_2$ (LGO) and multiple phases of Ga_2O_3 (GO) are prospective ultra-wide bandgap metal oxides for electronic and optoelectronic applications [1]. While both GO and LGO have recently been identified to most likely trap holes and which makes achievement of sufficient p-type conductivity difficult [2], LGO is particularly promising as a substrate for heteroepitaxial growth of GaN due to very small lattice mismatch (<1%), and a composite LGO/β-GO substrate has also been demonstrated [3]. Here, we provide a comprehensive study of the fundamental optical and phonon mode properties of high-quality single-crystals of LGO using generalized spectroscopic ellipsometry in combination with hybrid-level density functional theory calculations that covers the optical properties in the far-infrared to vacuum ultraviolet spectral range. In the mid- to far-infrared range, we identify all 33 infrared-active pairs of transverse and longitudinal optical phonon modes. We derive the anisotropic mid-band gap indices of refraction and static dielectric constants. In the visible to vacuum ultraviolet spectral range we identify band-to-band transitions and discuss near band-gap excitonic contributions. We compare the obtained results with the previous experimental and theoretical studies. [4,5,6]

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11:40am **EL+AS+EM-TuM-12 Optical and X-ray Characterization of Ge-Sn Alloys on GaAs***, **Haley Woolf**, C. Emminger, C. Armenta,* New Mexico State University*; M. Kim,* QuantTera*; S. Zollner,* New Mexico State University

In this undergraduate student presentation, we describe the optical and x-ray characterization of a thick $Ge_{1-y}Sn_y$ alloy grown on GaAs by chemical vapor deposition. From (224) x-ray reciprocal space maps we find that the alloy layer is grown pseudomorphically on the GaAs substrate. Therefore, we can use (004) rocking curves and reciprocal space maps to determine the alloy composition based on Vegard's Law. We find y=0.012.

For ellipsometry measurements, we first cleaned the surface ultrasonically with water and isopropanol to remove adsorbed organic overlayers and a portion of the native oxide. The remaining native oxide was found to be 2.6 nm thick. We then acquired the ellipsometric angles ψ and Δ from 0.5 to 6.5 eV photon energy and 60 to 75° incidence angle using a vertical variable angle of incidence ellipsometer (VASE) equipped with a computer-controlled Berek wave plate compensator. Due to the low tin content, these ellipsometric angles and the resulting pseudo-dielectric function could be described very well using a four-layer model, consisting of a GaAs substrate, a pure Ge layer, GeO_2 oxide, and air as the ambient. This results in an epilayer thickness of 1600 nm.

After fixing the thickness, we also obtained the dielectric function ε of the epitaxial $Ge_{1-y}Sn_y$ layer from a point-by-point fit. This is very similar to that of bulk Ge. The second derivative $d^2\varepsilon/dE^2$ was fitted with analytical line shapes to determine the critical point parameters of the alloy (amplitude, energy, broadening, and phase angle). The energy was compared with predictions from continuum elasticity theory based on established deformation potentials for Ge.

12:00pm **EL+AS+EM-TuM-13 Zinc Gallate ($ZnGa_2O_4$) Epitaxial Thin Films: Determination of Optical Properties and Bandgap Estimation Using Spectroscopic Ellipsometry***, S. Bairagi, J. Chang, C. Hsiao, R. Magnusson, J. Birch,* Linköping University, Sweden*; **Jinn P Chu**,* National Taiwan University of Science and Technology, Taiwan*; F. Tarntair,* National Yang Ming Chiao Tung University, Taiwan*; R. Horng,* National Yang Ming Chiao Tung University, Taiwan*; K. Järrendahl,* Linköping University, Sweden

Very high quality Zinc gallate (ZGO) epitaxial thin films were grown on c-plane sapphire substrates by Metal-Organic Chemical Vapor Deposition and investigated using Spectroscopic Ellipsometry (SE). Two or more samples were grown with identical growth conditions but different growth times to obtain samples with similar crystallographic and optical properties but different thicknesses. Their thickness, roughness and optical properties were then determined using a Multiple Sample Analysis (MSA) based approach in tandem by the regression analysis of the optical model and measured data for all samples. Another set of ZGO samples were grown for the same growth time but etched using ion-bombardment for different time durations to achieve different thicknesses. These samples were also analyzed by SE using MSA and it was observed that etching times of 1 – 4 minutes had no discernible impact on the material's optical properties. It was also observed that both sets of samples exhibited identical optical properties and thus could be described using the same optical model, thereby showcasing the robustness of the MSA model. Line shape analysis of resulting absorption coefficient dispersion revealed that ZGO exhibited both direct and indirect interband transitions. A modified Cody formalism was employed to determine their optical bandgaps, resulting in a direct bandgap of 5.07 ± 0.015 eV and indirect bandgap of 4.72 ± 0.015 eV. These values were compared to values obtained using other popular bandgap extrapolation procedures to find which technique resulted in the most linear line shape. In a subsequent study, the first set of samples was annealed to different temperatures and their optical properties were analyzed using SE. It was observed that the onset of absorption and hence the optical bandgap blue-shifted to higher photon energies as the annealing temperature was increased from 800° C to 1100° C. This was a consequence of inter-diffusion between the ZGO thin film and sapphire substrate, resulting in the formation of an epitaxial β-(Al, Ga)O intermediate layer between the two, and modification of ZGO to Zn(Al, Ga)O due to diffusion of Al. Post analysis it was observed that the formation of β-(Al, Ga)O intermediate layer began already at 800° C and led to an increase in the overall film thickness with increasing annealing temperatures. The direct and indirect optical bandgaps for the Zn(Al, Ga)O thin film were determined to be 5.10, 5.19, 5.73 eV and 4.80, 4.87, 5.45 eV for 800, 950 and 1100° C, respectively and the increase is attributed to the diffusion of Al from the sapphire substrate.

Fundamental Discoveries in Heterogeneous Catalysis Focus Topic
Room 321 - Session HC+AS+SS-TuM

Energetic Processes and Tailored Surfaces in Heterogeneous Catalysis

Moderators: Tim Schäfer, Georg-August Universität, Göttingen, Germany, **Arthur Utz**, Tufts University

8:40am **HC+AS+SS-TuM-3 Adsorption and Reaction of Acetic Acid on Single-Crystal and Faceted Nanoparticle Anatase $TiO_2(101)$ Surfaces***, C. O'Connor, R. Ma, Y. Wu, W. DeBenedetti, F. Gao, Y. Wang, G. Kimmel,* ***Zdenek Dohnálek,*** Pacific Northwest National Laboratory

Understanding the adsorption and reactivity of carboxylic acids on anatase TiO_2 is of great interest in catalysis for the potential synthesis of selective carbon-coupling reaction products. A comparative investigation of the adsorption and reaction of acetic acid on single-crystal planar and faceted nanoparticle anatase $TiO_2(101)$ surfaces was performed using a combination of infrared spectroscopy, temperature-programmed reaction spectroscopy and scanning tunneling microscopy. Acetic acid adsorbs as bidentate acetate and monodentate acetic acid dependent on the adsorption temperature as determined by infrared spectroscopy and scanning tunnelling microscopy measurements on single-crystal TiO_2 under ultra-high vacuum conditions. The adsorption of bidentate acetate has a saturation coverage of 0.5 ML. However, high-density phases containing a mixture of bidentate acetate and monodentate acetic acid and solely monodentate acetic acid occur at low temperature conditions. The sole presence of bidentate acetate is observed at elevated temperature due to the facile conversion of monodentate acetic acid to bidentate acetate and desorption of monodentate acetic acid which precludes investigating the reactivity of high-density phases under vacuum conditions. The presence of monodentate acetic acid persists to notably higher temperatures on the faceted nanoparticles than single-crystal TiO_2. The reaction of bidentate acetate produces ketene and water as determined by temperature-programmed reaction spectroscopy on single-crystal TiO_2. Notably, there is an absence of carbon-carbon coupled products, such as acetone, from the sole reaction of bidentate acetate. The selectivity of bidentate acetate is independent of coverage up to the saturation coverage. Similarly, the reaction of acetic acid on faceted nanoparticle TiO_2 produces predominantly ketene and water as determined by temperature-programmed reaction spectroscopy under low vacuum conditions. This study provides mechanistic insight into the reactivity and stability of surface-bound intermediates that are present for the reaction of acetic acid on anatase TiO_2 catalysts.

9:00am **HC+AS+SS-TuM-4 Phase Transformation of Single Micro-Sized TiO_2 Crystals***, W. Lu, H. Zhu, N. Craft, K. Park,* ***Zhenrong Zhang,*** Baylor University

Understanding the reactivity of various crystal faces in different polymorphs of TiO_2 in photoreaction is important for many photocatalytic applications. Here, we monitored and studied the anatase-rutile phase transition (ART) processes of individual micro-sized TiO_2 crystals from the pure anatase phase to the mixed-phase, then to the rutile phase. High-quality micro-sized anatase TiO_2 crystals with a large percentage of (001) facets were hydrothermally synthesized. Micro-Raman spectroscopy mapping and scanning electron microscope (SEM) images were obtained at different annealing stages to correlate the crystal structure transformation with the morphology change. The ART processes of individual anatase particles are distinctive and depend on the various defects which serve as rutile nucleation sites. Two types of transition pathways are observed. In one type of growth pathway, rutile nucleation was formed at a corner of an anatase crystal. The rutile phase then gradually propagated over the rest part of the microparticle. The phase concentration calculated from Raman spectra revealed that the ART transition follows the first-order reaction mechanism. In the other type of growth pathway, multiple rutile nucleation sites formed simultaneously on different edges and corners of the microcrystal. The rutile phase then spreads over the whole crystal from these nucleation sites forming multi-grain crystals.

9:20am **HC+AS+SS-TuM-5 Reactivity of Formic Acid on Single Atom Rh Supported on $Fe_3O_4(001)$***,* ***Christopher Lee****, M. Sharp, S. Smith, B. Kay, Z. Dohnálek,* Pacific Northwest National Laboratory

Single-atom catalysis is a growing area of research due to the potential to qualitatively transform the activity and selectivity of supported metal catalysts. However, the fundamental surface science studies of their unique properties have not been widely studied. Here we investigate the reactivity of formic acid on several model Rh catalysts, including single Rh adatoms, Rh incorporated into the support oxide lattice, and metallic Rh clusters on $Fe_3O_4(001)$ under ultrahigh vacuum conditions. The single Rh adatoms are found to be the most active towards CO_2 production, followed by incorporated Rh and then by Rh nanoclusters. While the reaction of formic acid with $Fe_3O_4(001)$ primarily results in CO desorption at ~570 K, the addition of small amounts of single adatom Rh (~0.01 Rh per $Fe_3O_4(001)$ unit cell (u.c.)) results in a dramatic shift towards CO_2 production at lower temperatures starting at 540 K and dropping to ~470 K at larger HCOOH coverages. The incorporated Rh system also yields CO_2 product, but it takes ~15-20 times as much Rh to achieve the same activity as the Rh adatoms. Rh nanoclusters exhibit reactivity similar to metallic Rh with low-temperature CO_2 and H_2 desorption at ~310 K while still producing substantial amounts of CO_2 at 450-500 K, not observed on pure $Fe_3O_4(001)$. These differences demonstrate that different forms of Rh supported on $Fe_3O_4(001)$ affect the reactivity of the catalytic surface beyond the local stabilized transition metal site. The stabilized adatoms turn over multiple adsorbates to products demonstrating the importance of spillover from the support oxide. Furthermore, the single Rh adatoms and incorporated Rh exhibit an intermediate activity distinct from metallic Rh nanoparticles or the $Fe_3O_4(001)$ substrate, demonstrating the additional degree of reactive tuning provided by single-atom catalysts. The similarity in reactive behavior between the Rh adatom and mixed Rh oxide systems hints toward a common mechanism between the systems. The much larger reactivity of the Rh adatom system suggests that under reaction conditions, a small amount of the mixed Rh oxide may be dynamically converted to Rh adatom and that the Rh adatom is responsible for the lower temperature CO_2 activity.

9:40am **HC+AS+SS-TuM-6 WO_3/Ag_2S type-II Hierarchical Heterojunction for Improved Charge Carrier Separation and Photoelectrochemical Water Splitting Performance***,* ***Jyoti Yadav****, J. Singh,* IIT DELHI, India

In the present work, WO_3/Ag_2S heterojunction was fabricated to achieve an improved photoelectrochemical (PEC) water splitting performance. To prepare the working electrodes,a two step method was adopted which includes, a thin film of WO_3 deposited using DC sputtering and a well-separated Ag_2S nanorods fabricated by glancing angle deposition,. The PEC response was studied for bare WO_3, Ag_2S, and WO_3/Ag_2S heterojunction. The as-prepared WO_3/Ag_2S heterojunction samples revealed higher absorption as well as higher photocurrent density of 2.40 mA/cm^2 (at 1V

Ag/AgCl) as compared to bare WO_3 thin film (0.34 mA/cm^2). The enhancement in the photocurrent density of WO_3/Ag_2S electrodes could be ascribed to the formation of the type-II heterojunction between WO_3 and Ag_2S which effectively separates and transfers the charge carriers at the interface. In addition, increased trapping of light due to vertically tilted Ag_2S nanorods structures results in an effective absorption of light. Furthermore, electrochemical impedance spectra measurements showed that WO_3/Ag_2S samples have lower charge transfer resistance at the semiconductor electrolyte interface with high flat band potential. The present work provides a deeper insight on the role of the interface formed between WO_3 and Ag_2S for the photoelectrochemical water splitting response.

11:00am **HC+AS+SS-TuM-10 Using Photon-Stimulated Desorption to Probe the Structure and Reaction Dynamics of Molecules Adsorbed on TiO_2(110)**, ***Greg Kimmel***, Pacific Northwest National Laboratory **INVITED**

TiO_2 is a widely used photocatalyst. Its ability to oxidize organic contaminants makes it useful, for example, in air and water purification systems and as a thin-film coating for self-cleaning surfaces. As a result of titanium dioxide's practical applications and its potential use in photocatalytic water spitting, it has been the subject of a tremendous amount of research. We have investigated the photon-stimulated reactions of small molecules, such as O_2, CO, and acetone, on rutile TiO_2(110). Experiments on clean, well-characterized single crystal surfaces, including azimuth- and angle-resolved measurements of photo-desorption products, provide key insights into the photochemical reactions of interest. This talk will highlight examples of this approach, including the photochemistry of chemisorbed O_2, the photo-oxidation of CO, and the photon-stimulated reactions of acetone. For the photo-oxidation of CO, the results show that a bridging O-O-C-O intermediate ejects CO_2 perpendicular to the bridging oxygen rows, which is consistent with density functional theory calculations. However, in contrast to earlier suggestions, the reaction kinetics show that the oxidation is a multi-step process. For acetone, the azimuth-resolved measurements of the methyl fragments revealed a second reaction channel that probably involves an enolate intermediate on the surface.

11:40am **HC+AS+SS-TuM-12 Comparison of Pt, Rh and Ir Single Atoms on a Fe_2O_3 Model Support**, ***Gareth Parkinson***, *A. Rafsanjani Abbasi, L. Puntscher, F. Kraushofer, P. Sombut, C. Wang,* TU Wien, Austria; *M. Meier,* University of Vienna, Austria; *M. Eder, J. Pavelec, G. Franceschi, M. Riva, M. Schmid, U. Diebold,* TU Wien, Austria; *C. Franchini,* University of Vienna, Austria

Understanding how the local environment of a "single-atom" catalyst affects stability and reactivity remains a significant challenge. Fe_2O_3 is the most common iron-oxide support material utilized for SAC, but little is known about how metal adatoms bind at its surfaces. In this talk, I will compare and contrast the behavior of Pt, Rh,[1,2] and Ir atoms on the flat, well-ordered (1×1) termination of Fe_2O_3(1-102).[3,4] Using a combination of scanning probe microscopy and spectroscopic data, as well as theoretical calculations, I will demonstrate significant differences between the adsorption site and thermal stability of the metals, as well as differences in their interaction with water and carbon monoxide.

[1] F. Kraushofer *et al.*, Single Atom Catalysts: Surface Reduction State Determines Stabilization and Incorporation of Rh on α-Fe_2O_3(1-102) (Adv. Mater. Interfaces 8/2021). *Advanced Materials Interfaces* **8**, 2170045 (2021).

[2] F. Kraushofer *et al.*, Single Rh Adatoms Stabilized on α-$Fe_2O_3(1\bar{1}02)$ by Coadsorbed Water. *ACS Energy Letters* **7**, 375-380 (2022).

[3] F. Kraushofer *et al.*, Atomic-Scale Structure of the Hematite α-Fe_2O_3(1-102) "R-Cut" Surface. *J. Phys. Chem. C* **122**, 1657-1669 (2018).

[4] G. Franceschi *et al.*, A Model System for Photocatalysis: Ti-Doped α-Fe_2O_3(1-102) Single-Crystalline Films. *Chem. Mater.* **32**, 3753-3764 (2020).

12:00pm **HC+AS+SS-TuM-13 HC Graduate Student Finalist Talk: Preparation and Characterization of Model Homotopic Catalysts: Rh Adatoms, Nanoparticles, and Mixed Oxide Surfaces on Fe_3O_{-4-}(001)**, ***Marcus Sharp***, PNNL/WSU; *C. Lee, M. Mahapatra, S. Smith, B. Kay, Z. Dohnálek,* PNNL

Single atom catalysts have emerged as a new catalyst frontier due to the need for improved catalyst activity and selectivity. Yet key fundamental challenges exist regarding understanding of how their activity and stability depend on their coordination environment. Surface science studies have the tools necessary to investigate such monodispersed single atom catalysts and their chemistry under well-controlled reaction conditions. Here, we have studied the behavior of Rh on the Fe_3O_4(001) single crystal surface using X-ray photoelectron spectroscopy (XPS), temperature programed desorption (TPD), and scanning tunneling microscopy (STM). We employ the Fe_3O_4(001) reconstructed surface that has been shown to stabilize single 2-fold coordinated metal adatoms to elevated temperatures. By varying the Rh deposition and annealing temperature, we have identified a series of model catalysts possessing unique Rh sites. These catalysts include Rh adatoms, mixed surface layers with octahedrally-coordinated Rh, small Rh clusters, and large Rh nanoparticles on both mixed and pure Fe_3O_4 surfaces. STM and XPS are used to characterize the Rh coverage, species, binding, and particle size distribution. Subsequently, CO and CO_2 adsorption is employed to characterize the chemical and redox properties of these sites. CO binds strongly with Rh adatoms, clusters, and nanoparticles desorbing at higher temperatures but interacts weakly with the Rh-octahedral species. In contrast, CO_2 interacts most weakly with Rh adatoms and nanoparticles, while interactions between Rh-octahedral and Fe-octahedral are indistinguishable. Further, CO_2 is used to distinguish between metallic Rh sites and Fe_3O_4(001) sites, which shows good agreement with our STM results. These model systems allow us to directly investigate reaction mechanisms on different types of catalytic sites furthering our understanding of how to selectively tune catalyst sites for desired reaction pathways. Future studies are directed toward understanding the energetics and reaction pathways of the hydrogenation of unsaturated hydrocarbons and carbonyl functional groups.

Mini Symposium on 2D Materials Synthesis
Room 303 - Session MS-2DMS+2D+EM+NS-TuM

Direct Growth of 2D Materials, Including CVD and MBE

Moderators: Matthias Batzill, University of South Florida, **Erica Douglas**, Sandia National Laboratories, **Maryam Ebrahimi**, Lakehead University, Canada, **Kathleen McCreary**, Naval Research Laboratory

8:00am **MS-2DMS+2D+EM+NS-TuM-1 Efficient Control of 2D Magnetism**, ***Cheng Gong***, University of Maryland **INVITED**

The recently discovered magnetic two-dimensional (2D) van der Waals materials [1, 2] provide ideal platforms to enable the atomic-thin, flexible, lightweight magneto-optical and magnetoelectric devices. Though many have hoped that the ultra-thinness of 2D magnets should allow an efficient control of magnetism, the state-of-the-art has not achieved notable breakthroughs to this end, with only proof-of-concept reports. There appear to be some fundamental obstacles for efficient control. In this talk, I will analyze the challenges and present our recent theoretical and experimental progress on efficient electrical and optical control of 2D magnetism [3-7]. We envision the efficient control of 2D magnets could open new avenues for the low-power spintronics and photonics.

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8:40am **MS-2DMS+2D+EM+NS-TuM-3 Epitaxial Growth of Transition Metal Dichalcogenide Monolayers for Large Area Device Applications**, *J. Redwing,* ***Thomas V. Mc Knight***, The Pennsylvania State University **INVITED**

Wafer-scale epitaxial growth of semiconducting transition metal dichalcogenide (TMD) monolayers such as MoS_2, WS_2 and WSe_2 is of significant interest for device applications to circumvent size limitations associated with the use of exfoliated flakes. Epitaxy is required to achieve single crystal films over large areas via coalescence of TMD domains. Our research has focused on epitaxial growth of 2D semiconducting TMDs on c-plane sapphire substrates using metalorganic chemical vapor deposition (MOCVD).Steps on the miscut sapphire surface serve as preferential sites for nucleation and can be used to induce a preferred crystallographic direction to the TMD domains which enables a reduction in twin boundaries in coalesced films. The step-directed growth is dependent on the surface termination of the sapphire which can be altered through pre-growth annealing in H_2 and chalcogen-rich environments. Uniform growth of TMD monolayers with significantly reduced inversion domains is demonstrated on 2" diameter c-plane sapphire substrates enabling large area transfer of monolayers for characterization and device fabrication and testing.Applications for wafer-scale TMD monolayers in nanoelectronics, sensing and photonics will be discussed.

9:20am **MS-2DMS+2D+EM+NS-TuM-5 Formation of Transition Metal Dichalcogenide Janus Monolayers and 2D Alloys Through Non-Equilibrium Synthesis and Processing Approaches***, **Kai Xiao**, S. Harris, Y. Lin, C. Liu,* Center for Nanophase Materials Sciences, Oak Ridge National Laboratory*; G. Duscher,* University of Tennessee Knoxville*; M. Yoon,* Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA*; L. Liang, C. Rouleau, A. Puretzky, D. Geohegan,* Center for Nanophase Materials Sciences, Oak Ridge National Laboratory

Doping and alloying in 2D materials are efficient ways to tune the optical and electronic properties, induce new crystal structures and phases, and add new functionalities. In this talk, I will introduce how to precisely tailor the doping of 2D TMDs using non-equilibrium synthesis and processing techniques including chemical vapor deposition and hydrothermal laser implantation. By tailoring isoelectronic doping of chalcogens and metals in 2D TMDs (e.g., $MoSe_2$, WS_2) during CVD synthesis, the uniform alloys, gradient alloys, and lateral heterostructures are controlled grown on substrates which exhibit many novel properties including tunable bandgaps, enhanced photoluminescence, modulated charge carriers, etc. I will also describe a novel PLD approach with in situ diagnostics such as Raman and photoluminescence to sensitively tune the kinetic energies of Se clusters (3-5 eV/atom) to selectively implant Se atoms within monolayer WS_2 and MoS_2 crystals to form novel Janus WSSe and MoSSe monolayers. Synthesis science was supported by the U.S. Dept. of Energy, Office of Science, Materials Science and Engineering Division. This work was performed at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.

9:40am **MS-2DMS+2D+EM+NS-TuM-6 Effects of Deposition Technique on Monolayer MoS_2 and WS_2***, **Ama Agyapong**, S. Mohney,* Pennsylvania State University

It is important to understand how the deposition of metal contacts affects two-dimensional transition metal dichalcogenides (TMDs) so that we can successfully integrate TMDs into next-generation electronic and optoelectronic devices. This study employs Raman spectroscopy as a non-destructive method to probe structural changes induced by depositing metals on monolayer MoS_2 and WS_2. Differences between electron-beam evaporated and DC magnetron sputtered metal/MoS_2 and metal/WS_2 samples were observed in Raman spectra obtained through a transparent substrate using a backside geometry. The disappearance of characteristic Raman modes of the TMDs indicates structural disorder, as observed for sputtered In, Pd, and Pt films on both monolayer MoS_2 and WS_2. This disorder is introduced even though the metals are not reactive with the TMDs. On the other hand, Raman modes remain if the metals are e-beam evaporated. The mass of the metal atoms appears to impact the structural disorder caused by sputtering, as characteristic MoS_2 and WS_2 modes are preserved (albeit with some changes to the spectra) when lighter metal atoms (Cu and Al) are sputtered. The results of this work provide insight on structural changes at the metal/TMD interface that may not be easily detectable in bulk TMDs, and we conclude that e-beam evaporation is a less destructive deposition technique for forming metal contacts on 1L TMDs than sputtering.

11:40am **MS-2DMS+2D+EM+NS-TuM-12 The Growth of $Nb_{1+x}Se_2$ by Molecular Beam Epitaxy***, **Peter Litwin**, S. Jaszewski, J. Ihlefeld, S. McDonnell,* University of Virginia

$NbSe_2$, a metallic transition metal dichalcogenide, has been the focus of numerous recent scientific studies due to the coexistence of superconductivity and charge density wave states it exhibits at low temperature. While less studied, this material also exists in a metal rich, Nb-intercalated (self-intercalated) phase in which additional Nb atoms populate the van der Waals gap. The self-intercalated phase, $Nb_{1+x}Se_2$, has been studied in the bulk form since the 1960's when it was synthesized by chemical vapor transport techniques; however, thin film synthesis of this material is rarely reported. Here we report on the growth of few layer $Nb_{1+x}Se_2$ by molecular beam epitaxy (MBE). We demonstrate that the degree of Nb-intercalation can be tuned through alteration of the Se to Nb flux ratio used during growth. Interestingly, we find that Nb-intercalation exists in all multilayer films, even under Se to Nb flux ratios as high as 45,000:1. The presence of Nb-intercalation results in an expansion of the material's c-axis lattice parameter which we measure using ex-situ x-ray diffraction (XRD). Chemical analysis of the grown thin films is carried out using in-situ x-ray photoelectron spectroscopy (XPS) and further confirms the Nb-rich nature of the grown thin films. The in-plane electrical conductivity is measured using a 4-point probe measurement tool and shows an inverse relationship with the Se to Nb flux ratio used during growth. Lastly, we also report on the thickness scaling of the material's electrical conductivity down to few-layer thick $Nb_{1+x}Se_2$ thin films.

12:00pm **MS-2DMS+2D+EM+NS-TuM-13 Formation of 1D and 2D Carbon-Based Nanomaterials on Surfaces***, **Maryam Ebrahimi**,* Lakehead University, Canada

On-surface reactions offer a platform to design molecular-based low-dimensional nanomaterials whose chemical and electronic properties can be tailored by their chemical structure. The molecules' functional groups and the reactivity of the substrates control the molecule-molecule and molecule-substrate interactions, which steer the design of the obtained molecular structures.We present various surface reactions for creating 1D and 2D polymers, metal-organic networks, and organometallic structures on Au(111), Ag(111) and Cu(111).To identify their topography and chemical nature, we employ scanning tunnelling microscopy and non-contact atomic force microscopy, and other surface characterization techniques, such as X-ray photoelectron spectroscopy, complemented with density functional theory calculations.

The chemical and thermal stability and structural design of these molecular-based low-dimensional nanomaterials make them promising candidates for various applications. These materials are tailored to exhibit unique electronic properties, charge mobility and/or electron spin-based structure, suitable for carbon-based nanoelectronics, spintronics, and quantum technology applications.

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Plasma Science and Technology Division
Room 305 - Session PS1+NS-TuM

Advanced Plasma Patterning: EUV-Based, Multipatterning and Alternative Patterning Approaches (Imprint, DSA, Etc.)

Moderators: Yohei Ishii, Hitachi High Technologies America Inc., **Angelique Raley**, TEL US

8:00am **PS1+NS-TuM-1 EUV Patterning: Plasma Processing Innovations for Single Exposure and Multi-Patterning***, **Katie Lutker-Lee**,* TEL Technology Center, America, LLC **INVITED**

As extreme ultraviolet (EUV) lithography progresses to a mature high volume manufacturing technology, innovations are still required to meet the device scaling and performance requirements. While many of these innovations may take the shape of integration changes, plasma processing will still play an important role in shaping the next generation of technology. In order to advance plasma processing for the next nodes, we must start looking at plasma process development beyond the standard process tuning knobs. New chemistries and techniques must be thoroughly investigated and out of the box thinking must be applied. The applications to which plasma processing can benefit single exposure and multi-patterning techniques are vast, ranging from roughness and profile improvements to the enablement of new integrations techniques.

In this presentation, we will discuss a few of the many innovations we have investigated to overcome the challenges of EUV patterning. It is well known that EUV lithography suffers from stochastically driven defectivity, in particular, feature breaks and bridges, and high roughness.[1] Plasma based process improvements, including etch process co-optimization with films, and selective deposition, have provided critical improvements in this area.[2,3] Processes such as selective deposition also open the door for innovative integration schemes that would otherwise be inhibited.[4] The advent of high-NA EUV lithography will present its own unique challenges, including new materials, in particular metal containing resists, and even smaller feature sizes, in addition to the known challenges of the current generation of EUV lithography.[5] Advanced plasma processing, especially etch, will play an important role in overcoming these hurdles.

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8:40am **PS1+NS-TuM-3 Reduction of EUV Resist Damage by using Neutral Beam Etching**, *N. Soo,* School of Advanced Materials Science and Engineering, Sungkyunkwan University, Republic of Korea*;* ***Geun Young Yeom,*** School of Advanced Materials Science and Engineering, Sungkyunkwan University / SKKU Advanced Institute of Nano Technology (SAINT), Sungkyunkwan University, Republic of Korea

Even though Extreme Ultra Violet (EUV) lithography has the advantage of implenting a finer pattern compared to ArF immersion lithography due to the use of 13.5 nm instead of 193 nm as the wavelengh of the light source, due to the low energy of EUV light source, EUV resist has a thinner thickness than conventional ArF resist and it is more vulnerable to radiation damage received during the etching because of its low etch resistance and also tends to have a problem of low etch selectivity. In this study, the radiation damage to an EUV resist during the etching of hardmask materials such as Si_3N_4 and SiO_2 using a CF_4 neutral beam has been investigated and the results were compared with those etched by a CF_4 ion beam. The results showed, for the etching of the same EUV resist thickness, less line edge roughness, less critical dimension loss, and higher etch selectivity to the hardmask materials such as SiO_2 and Si_3N_4 were obtained for the CF_4 neutral beam etching compared to the CF_4 ion beam etching.

Key word : extreme ultraviolet (EUV) lithography, extreme ultraviolet (EUV) PR, low damage, line edge roughness (LER), critical dimension (CD), neutral beam etching(NBE), ion beam etching(IBE)

9:00am **PS1+NS-TuM-4 Numerical Investigation of EUV Induced H_2-O_2 Plasmas and Surface Chemistry**, ***Tugba Piskin,*** University of Michigan*; V. Volynets, S. Nam,* Mechatronics Research, Samsung Electronics Co., Ltd, Republic of Korea*; H. Lee,* Mechatronics Research, Samsung Electronics Co., Ltd., Republic of Korea*; M. Kushner,* University of Michigan

Extreme Ultra-Violet (EUV) systems achieve smaller feature sizes in microelectronics processing by deploying photons with ~10 nm wavelength for photolithography. There are several advanced techniques for generating EUV photon beams; one of which is ablating and ionizing tin droplets with pulsed lasers. Excited tin ions emit photons with a 13.5 nm wavelength. These photon beams are collected and focused with a collector mirror, and then photons are transferred to the scanner unit. The lifetime and reflectivity of the collector mirror decline with time due to deposition of tin. An in-situ cleaning technique of tin deposited on the optics involves pumping H_2 into the chamber. H_2 gas does not substantially attenuate the EUV beams, but the photons have enough energy (92 eV) to create an H_2 plasma through photoionization and photodissociation reactions. Hydrogen radicals then etch the tin deposits by producing stannane, a volatile gas which can be pumped from the chamber. The most significant loss mechanism for hydrogen radicals is recombination reactions on the walls. The addition of a small amount of oxygen helps decrease the wall losses of hydrogen radicals by production of the water vapor. The water vapor adsorbs on surface sites, which blocks recombination of H atoms.

In this paper we discuss results from a computational investigation of the low-pressure H_2-O_2 plasma produced from EUV photon beams in a generic EUV photolithography tool using the Hybrid Plasma Equipment Model (HPEM). The densities of radicals, ions, and excited species, their fluxes (including energy-and-angular distributions) to the chamber walls, and the surface coverage fractions will be discussed. For pressures of a few to tens of Pa and hundreds of Watts EUV power, the addition of oxygen increases hydrogen radical density in the chamber and decreases the surface loss of hydrogen radicals. The consequences of oxygen fraction, pressure, and photon intensity on plasma properties and surface mechanisms will be discussed.

Work supported by Samsung Electronics and the National Science Foundation.

9:20am **PS1+NS-TuM-5 Modeling of Shallow Trench Isolation Etch in Self-aligned Double Patterning Process*, Shuo Huang*,** *P. Panneerchelvam, C. Huard,* KLA Corporation*; S. Sridhar, P. Ventzek,* Tokyo Electron America*; M. Smith,* KLA Corporation

As the critical dimensions (CDs) decrease to a few nanometers while the aspect ratios increase beyond 100, the cost of process development significantly increases and the performance of the plasma etch process is critical to the success of ramping a new technology node toward profitable high-volume manufacturing. In this paper, a plasma dry etch simulator developed at KLA, ProETCH® [1], has been applied to investigate a defect that arises in an overlay metrology target in DRAM during shallow trench isolation (STI) etch patterned using self-aligned double patterning (SADP). SADP process is characterized by performing lithography at a pitch that is two times larger than the desired pitch and is followed by spacer deposition, a spacer etch-back and core etch processes. A challenge of this scheme is that each process introduces some non-uniformity, leading to variations in, for example, the hard mask that is eventually utilized for the final etch. One typical defect is the pitch walk, which manifests different trench openings between the pillars. This periodicity is indicative of the SADP process and corresponds to where the resist core line is patterned initially. The principal objective of this work is to investigate the influence of hard mask irregularities on the STI etch process evolution ProETCH. The mechanism of silicon etch by Ar/Cl_2 plasma was developed with the experimental data (cross-section SEM images) as reference. The variations in the hard mask that arise during the SADP process were found to have a significant impact on the printability of these targets. The differences in trench openings result in aspect ratio dependent etch (ARDE), which could be mitigated by modulating the plasma fluxes to the surface.

[1] P. Panneerchelvam et al., Trilayer hard mark lithography and etch for BEOL manufacturing, SPIE Advanced Lithography, San Jose, California, USA, April 2022.

9:40am **PS1+NS-TuM-6 Polymer Engineering for High Aspect Ratio Plasma Etching Enabled by Chemistry*, Phong Nguyen*,** *S. Biltek, X. Guo, N. Nathan Stafford,* American Air Liquide

High aspect ratio (HAR) ONON channel etch is a very complex and challenging step in 3DNAND flash memory production and the challenges increase with increasing vertical stack height and reducing pitch sizes. A variety of fluorocarbon gases are used to etch the alternating layers of SiO2 and SiN selective to the mask while maintaining a vertical profile. Control of sidewall polymer formation and its properties such as electrical conductivity are potential pathways to overcome undesirable patterning feature distortions such as bowing, twisting, tilting, and sidewall electrostatic interference i.e "charging."

We demonstrate that engineering the polymer for both its composition as well as conductivity can be accomplished by modification of the chemistry mixture that is used in the plasma process. Characterization of the polymer is done using XPS, SEM, EDS, and current-voltage (I-V) measurements in a variety of simplified test structures to elucidate the properties of the polymer on the etch front and the sidewall. Understanding of the composition of polymers from standard fluorocarbon chemistries including C4F8 and C4F6 along with new fluorocarbons gases will be presented showing changes in the C/F ratio of the polymer on the sidewall at different aspect ratios as well as the difference in polymer between the etch front and the sidewall of test structures. In addition, Quadrupole Mass Spectrometry (QMS), a powerful tool, is implemented to identify positive ion fragments that might be present inside the plasma. Furthermore, such details can elucidate the deposition and etching characteristic of these ions during HAR etching. The combination of polymer characterization and analysis of gas species via QMS can give us a better understanding of the etching process. Finally, new work in improvement of the polymer conductivity using new etching gases will be presented demonstrating >100x improvement in the polymer conductivity.

11:00am **PS1+NS-TuM-10 Achieving Better Etching Performance with Lower GWP Gases*, Nicolas Gosset*,** *T. Hasegawa, V. Gamaleev,* Air Liquide Laboratories, Japan **INVITED**

Nowadays, new architectures and structures for advanced Logic and Memory devices come with new etching processes and challenges. Among them, anisotropic etching of Si dielectric layers with very high selectivity to the mask, defect free soft-landing to the under layers, and profile control (no bowing, twisting, scalloping, clogging, loss in critical dimensions, and etch stop) is needed for the realization of advanced patterns (e.g. gate spacers, SADP, SAQP, high aspect ratio ONON and contact holes). These layers, such as SiO_2 and SiN, are standardly etched using fluorocarbon-based plasmas that involve multiple simultaneous reactions and phenomena. A key one is passivation, used to suppress lateral etching and damages. Etchants such as CF_4, C_4F_8, C_4F_6, CHF_3, CH_3F, etc. allows the etching of SiO_2 and SiN through the generation of mixed and polymer layers which, assisted by ions bombardment, lead to desorption of volatile byproducts such as CO_x, COF_x, SiF_x, NH_x and HCN. Same polymers generated by these standard gases are also used to protect structure' sidewalls during the etching, where the contribution of ion bombardment is much weaker. Nevertheless, the lack of polymer conformality on the sidewall and its different interactions with the mask or under layer materials strongly contribute to the appearance of etching defects that need to be mitigated.

To mitigate these drawbacks, we investigated the potential of new hydrofluorocarbons-based gases for the etching of high aspect ratio structures, such as 3D NAND holes or DRAM pillars, as well as gate spacers. Not only do these new etchants outperform the ones currently used (higher selectivity to the mask, better profile control, etc.) but they are also more environmentally friendly with lower Global Warming Potentials (GWP). In-depth studies (e.g. polymer deposition, composition, OES, etc.) have shown that these improved performances are linked to the unique polymerization properties of the molecules on the mask and structure sidewalls. The observed differences in profiles etched by two isomers demonstrate the importance and impact not only of the chemical composition but also the molecule structure and design on etch performances. In this example, a first isomer leads to more polymer deposition on the bottom of HAR holes, while polymer generated by a second isomer deposits more on the top. A second example, using a similar approach, demonstrates how the usage of new hydrofluorocarbons in Plasma-Enhanced Atomic Layer Etching process allow reducing SiN spacers footing with a soft-landing on Si channel. Utilizing these lower GWP gases lead to a process with better profile control and similar throughput.

11:40am **PS1+NS-TuM-12 Etch Profile Control for High-Aspect-Ratio Amorphous Carbon Mask Layer Etching*, Du Zhang*,** *S. Chang, P. Luan, M. Wang,* TEL Technology Center, America, LLC

The etch profile control for the amorphous carbon layer (ACL) is an important step for the 3D NAND fabrication process. Because ACL is the mask material for defining the pattern of the high-aspect-ratio-contact (HARC) dielectric ONON layer etch process, the precise control of its etch profile is necessary. Specifically, an ideal ACL mask profile should be free of symptoms such as hole circularity distortion, profile twisting, bowing, and undercutting. In order to achieve this desired etch performance, knowledge of various etch contributing factors must be systematically derived and applied, including etch surface chemistry, high-aspect-ratio (HAR) etchant transport, ion flux and ion energy angle distribution function (EADF) control, etc.

In this work, we investigate the ACL etch fundamental characteristics through combined 2D chamber-scale plasma simulations with the hybrid plasma-equipment model (HPEM) and 3D etch profile simulations with the Monte-Carlo Feature Profile Model (MCFPM) for an inductively-coupled-plasma (ICP) reactor with RF bias (detailed descriptions of the simulation tools are discussed in M. Wang and M. J. Kushner. J. App. Phys. 107, 023309 (2010)). In particular, we focus on the profile trends under different reactant fluxes and energies. Our findings indicate that maintaining a neutral-starved (ion-rich) etch regime is essential for the mitigation of both the channel hole etch circularity distortion and the slit etch profile twisting. To achieve this desired etch regime, the HAR ion and neutral transport must controlled by the RF bias power and frequency, substrate temperature, etc. Furthermore, especially in this neutral-limited etch regime which is necessary for distortion and twisting mitigation, the control of the consequent aspect-ratio dependent etching (ARDE) as well as maintaining the critical dimension (CD) and reducing bowing and undercutting are also necessary. For this purpose, atomistic density functional theory (DFT) calculations have been applied to compare the reaction energetics for various ALD-like sidewall passivation chemistries. Specifically, we propose a new process based on its favorable reaction energetics. Experimental cross-section images have matched simulation results. In conclusion, our insights have provided guidance for process optimization and tool design to meet the industrial demands.

12:00pm **PS1+NS-TuM-13 A Mask-free and Contactless Plasma Patterning Technique for Interdigitated Back Contact Silicon Heterojunction Solar Cells Fabrication*, Junkang Wang*,** *M. Ghosh, P. Bulkin, D. Daineka, P. Roca i Cabarrocas,* LPICM-CNRS, École Polytechnique, Institut Polytechnique de Paris, France*; S. Filonovich,* TotalEnergies GRP, France*; J. Alvarez,* Laboratoire de Génie Electrique et Electronique de Paris, CNRS, CentraleSupélec, Université Paris-Saclay, France*; E. V. Johnson,* LPICM-CNRS, École Polytechnique, Institut Polytechnique de Paris, France

Benefiting from the interdigitated back contact (IBC) architecture and the silicon heterojunction (SHJ) technology, IBC-SHJ solar cell currently holds the record efficiency for single-junction solar cells based on crystalline silicon [1]. However, the necessity of performing photolithographic patterning steps to form the interdigitated carrier collection zones makes this architecture unsuitable for low-cost, high-throughput manufacturing processes.

We present here a novel method that allows the creation of the interdigitated carrier collection zones for IBC-SHJ solar cells by PECVD process in a maskless and contactless manner. This method involves using a slottedpowered RF electrode, which has parallel slits in it, in a custom-designed CCP-PECVD chamber. By keeping the RF electrode in close proximity to the substrate surface (down to sub-mm range), plasma will selectively light only within the slits, thus mimicking the patterns on the electrode [2]. Deploying this patterned plasma process with an etching gas mixture (NF_3/Ar) on a well-designed silicon thin film stack, the interdigitated carrier collection zones required for an IBC architecture have been obtained.

Multiple structural and electrical characterizations (profilometry, spectroscopic ellipsometry, photoluminescence, photovoltage mapping, and secondary ion mass spectroscopy) are performed throughout the whole process flow, which gives good guidance for the processes optimization. The J(V) characteristics of the solar cells fabricated by this method will be presented, and the importance of an additional step to remove the damaged layer on the surface left by the patterned etching process will also be discussed.

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Plasma Science and Technology Division
Room 315 - Session PS2+MS-TuM

Modelling of Plasmas and Plasma Driven Processes, and Machine Learning

Moderators: Mingmei Wang, Lam Research Corporation, **David Lishan**, Plasma-Therm LLC

8:00am **PS2+MS-TuM-1 Molecular Dynamics Simulation of Oxide and Nitride Etching by CF_3^+ and Cl^+*, Charisse Marie Cagomoc*[1],** *S. Taira, M. Isobe, T. Ito, K. Karahashi,* Osaka University, Japan*; L. Belau, E. Hudson,* Lam Research Corporation*; S. Hamaguchi,* Osaka University, Japan

High-aspect-ratio (HAR) etching is one of the key processes in the fabrication of 3D NAND flash memory devices. HAR etching requires the formation of an etched hole channel hole with a high aspect ratio through all deposited films such as silicon dioxide (SiO_2) and silicon nitride (Si_3N_4). By having a high aspect ratio, more memory cells can be integrated into a single device, thereby increasing its storage capacity. However, the difficulty in creating a perfect hole profile increases as the aspect ratio increases. As such, this study aims to investigate and understand the surface reaction mechanisms involved in the HAR etching process. In this study, molecular dynamics (MD) simulations and ion beam experiments

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[1] **PSTD Coburn & Winters Student Award Finalist**

were used to analyze HAR etching processes, especially those of SiO_2 and Si_3N_4 etching by energetic (up to 6keV) CF_3^+ ions as CF_3^+ ions are typical reactive ions emitted from fluorocarbon plasma. Etching simulations of SiO_2 and Si_3N_4 multilayers (ONO) used in 3D NAND by incident CF_3^+ ions were also performed. The results showed that, at low energies, the etch rates observed in the multilayer were similar to those of individual materials, as expected. However, it was observed that the change in the rate occurred before the etching passed through the initial height of the interface. At high energies, a mixing of the oxide and nitride layers became significant and, when the thickness of each layer was thinner than the ion penetration depth, a single etch rate was observed throughout the multilayers. We also performed SiO_2 and Si_3N_4 etching simulations with simultaneous injections of energetic Cl^+ and CF_3^+ ions, which represents ion irradiation from Cl containing fluorocarbon plasmas. The interplay between Cl^+ and CF_3^+ ions for the etching reactions will be discussed.

8:20am **PS2+MS-TuM-2 Molecular Dynamics Simulations of High-Energy Ion Bombardment ALE Processes for Smooth Surfaces***, **Joseph Vella,*** Princeton Plasma Physics Laboratory*; D. Humbird,* DWH Consulting*; D. Graves,* Princeton Plasma Physics Laboratory, Department of Chemical and Biological Engineering Princeton University

Atomic-layer etching (ALE) has emerged as a promising technology in the semiconductor industry in order to continue to shrink the size of advanced electronics. ALE differs from other etching processes in that a substrate is etched by two steps: a surface modification step and a removal step. These steps are separated either in space or in time.[1] Both of the ALE steps have several parameters that can be varied which may lead to different results. For example, recently it has been demonstrated in a silicon-chlorine-argon ALE cycle, that a removal step with higher argon ion energies (>500 eV) and shorter exposure times (~0.2 s) yield smoother surfaces when compared to a corresponding cycle with lower ion energies (<80 eV) and longer exposure times (~5 s).[2] The reason for these results is not entirely understood. In this work, we use classical molecular dynamics (MD) in order to provide atomistic-level insight behind this phenomenon. We have previously demonstrated the ability of classical MD to accurately reproduce experimental silicon-chlorine-argon ALE data.[3] However, in the aforementioned work we focused on a bombardment step with argon ion energies only up to 100 eV. In this work, we extend our simulations to include higher argon ion energies and use the results to explain why high energy ion bombardment with short exposure times yield smooth surfaces.

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8:40am **PS2+MS-TuM-3 Analysis of RF Sheath Dynamics in Dual-Frequency Capacitively Coupled Ar Plasmas Using a Two-Dimensional Particle-in-Cell Simulation***, **Ji Hyun Shin,** H. Kim, C. Kim, S. Choi, H. Lee,* Pusan National University, Republic of Korea

With dual-frequency (DF) driving, ions' energy and flux can be controlled by high-frequency (HF) and low-frequency (LF) voltage waveforms, of which periods are faster and slower than ion transit time, respectively. DF capacitively coupled plasmas (CCP) are widely used in semiconductor etching processes because of effective ion energy control. In addition, various types of electrode structures are requested to improve the uniformity of the ion flux to the wafer. In this presentation, we report the effect of the electrode and the dielectric structure under DF driving conditions. The large computation load in two-dimensional particle-in-cell (PIC) DF CCP simulation was overcome using a parallelization with a graphics processing unit (GPU). We observed the time-dependent sheath dynamics with the change in structure to find a way to improve the spatial uniformity of the ion flux. The low-frequency driving enhances the plasma density in the peripheral region by the inward ion transport and improves the spatial uniformity of ion flux on the wafer. The ion transport is also controlled by the dielectric structure.

9:00am **PS2+MS-TuM-4 Incorporation of Match timing in a Global Plasma Circuit Model***, **Carl Smith,*** North Carolina State University*; S. Nam, K. Bae, J. Lee,* Samsung Mechatronics R&D Center, Republic of Korea*; S. Shannon,* North Carolina State University

Pulsed inductively coupled plasmas have been of interest over the past couple of decades due to reduced charge buildup [1], improved etch uniformity [2], and enhanced control over plasma chemistry [3]. Control over transients in n_e *and* T_e has been of keen interest in semiconductor processes where control over the duty cycle and pulse length have useful in controlling time averaged plasma parameters by continuously operating outside of steady state conditions.

One method of transient control that has been demonstrated is match timing, where the match is selectively tuned to deliver power at a specific point in the ON-Cycle, leveraging electrical impedance mismatch due to plasma transients to control the rate of power delivery and charged particle formation in the plasma. Control over dn_e/dt in an Argon discharge has been measured in a cylindrical inductively coupled reactor and compared against a Matlab based Global Plasma Circuit Model (GPCM) with good agreement. GPCM couples plasma parameters to an equivalent circuit model where match feedback has been accounted for. Control over power delivery at requested match points has been achieved through the incorporation of integrated match feedback and subsequent time dependent power delivery to the plasma. Modulation of the electron temperature spike in the early ON-Cycle has been observed in GPCM via match setpoint control. Matching model results with experimental results required particular attention to the effective area of the plasma (A_{eff}) and treatment of the plasma skin depth and will be presented. Center-point time-resolved electron densities were taken with a hairpin resonator probe while time-resolved power measurements from the matching network are taken with directional couplers placed at the matching network input port.

This work is supported by the North Carolina State University and the Samsung Mechatronics R&D Center.

9:20am **PS2+MS-TuM-5 Nanosheet GAA Transistor Manufacturing Modeling Study: Build Fundamental Knowledge of SiGe to Si Selective Etching in ClF_3 Gas***, **Yu-Hao Tsai,** M. Wang,* TEL Technology Center, America, LLC **INVITED**

The gate-all-around field-effect transistor (GAAFET) is a promising candidate for improving the performance of MOSFET beyond FinFET. Manufacturing the Si-SiGe stacked nanosheet GGAFET involves the highly selective SiGe and Si etching, in order to create the uniform inner spacers required for robust device performance. To achieve the ultrahigh selectivity, fundamental understandings of the origin of the selectivity in the process is crucial. We conduct an atomic-level investigation on how Ge atom impacts on the SiGe etching rate. The plasmaless dry etching process in ClF_3 gas is considered in this study. We perform the density functional theory (DFT) to model the elementary reactions of etchant molecule fluorinating Si/Ge atom. Based on the modelling results, the activation energy (E_a) of single-F-transfer breaking Ge-Ge bond is 0.4 eV lower than the Si-Si bond, with the E_a of Si-Ge cases fall between. The overall smaller E_a suggests that the relatively active fluorination reaction enabled by Ge atom facilitates the selective etching. In addition, a unique double-F-transfer from ClF_3 is identified, which simultaneously fluorinates two adjacent Ge atoms. The reaction enhances the selective etching with the drastically lowered E_a and more negative total energy change. We modelled different locations of Ge atom with respect to the fluorinated Si atom. The results show that the effect of Ge atom on lowering the Si fluorination E_a has a long-range nature. The calculation predicts a reduced E_a even when the Ge atom is on the second-nearest-neighbor site to the fluorinated Si atom. The finding implies that the Ge-induced E_a reduction can continuously assist the selective etching with a Ge-percentage as low as 6 at. %. Details of the surface chemical reactions and byproducts formation are discussed in the report.

11:00am **PS2+MS-TuM-10 Study on Spatiotemporal Evolution of Plasma Arcing in Low-Temperature Plasma***, **Si-jun Kim,** C. Cho, M. Choi, Y. Lee, I. Seong, W. Jeong, Y. You,* Chungnam National University, Republic of Korea*; J. Lee,* Samsung Electronics Co., Inc., Republic of Korea*; S. You,* Chungnam National University and Institute of Quantum Systems (IQS), Republic of Korea

Since arcing is a ubiquitous phenomenon in high-voltage applied systems and marks damages on surfaces where arcing arises, it has attracted attention from research fields as well as industries. Its formation mechanisms however have not been fully understood yet, especially under low-temperature plasma environments. Recently, we have reported electrical and optical characteristics of arcing, especially the observation of light emission from arcing occurred early than arcing current initiation under low-temperature plasma and brief explanations about formation mechanisms of this prior light. In this research, to elucidate the mechanism deeply, we analyzed a spatiotemporal behavior of arcing with a high-speed camera with various conditions (radio frequency (rf) power and voltage of an arcing inducing probe (AIP)). We found dependency of surface and bulk emission regions on the conditions; those regions are characterized by light emission positions on the AIP. In this talk, an improved arcing formation mechanism based on spatiotemporal analysis is discussed.

11:20am **PS2+MS-TuM-11 Instabilities in Low Pressure Magnetized Capacitively Coupled Plasmas***, **Sathya Ganta**, K. Bera, S. Rauf,* Applied Materials, Inc.*; I. Kaganovich,* Princeton University Plasma Physics Lab*; D. Sydorenko,* University of Alberta, Canada*; A. Khrabov, T. Powis,* Princeton University Plasma Physics Lab*; L. Xu,* Ruhr Universität Bochum, Germany

Low pressure (< 50 millitorr) capacitively coupled plasmas are commonly used for etching and deposition in the semiconductor industry. The plasma transport at low pressures is high causing significantly non-uniform steady state plasma density profiles. Static magnetic field is one option that can be used to improve plasma uniformity **[1]**. With the appropriate magnetic field profile, one can improve spatial uniformity in plasma density or adjust the plasma density profile to one that is desirable for the processing application. However, at high magnetic field intensity and low gas pressures, instabilities have been observed in plasmas which change the transport coefficients of electrons. This has been reported before by Boeuf **[2]**. In this paper, we examine such instabilities using a 2-dimensional particle-in-cell plasma simulation where plasma particle kinetics equations are coupled with the Poisson equation solver while incorporating a high intensity external static magnetic field. The code has been developed at the Princeton Plasma Propulsion Laboratory (PPPL). Using the code, Argon only capacitively coupled plasma simulations are performed at different process conditions (e.g., pressure, RF voltage), and for different intensities of external magnetic field. The simulation results for varying magnetic field intensities and for various processing conditions are analyzed to elucidate the physical reason behind the magnetic field induced plasma instability.

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11:40am **PS2+MS-TuM-12 2D Hybrid Simulation of a CF4 Plasma in a DF CCP Reactor: Influence of Operating Conditions on Plasma Bulk Properties and Fluxes on the Wafer***, **Pierre Ducluzaux**,* LTM/CNRS-UGA, France; STmicroelectronics, France*; D. RISTOIU,* STmicroelectronics, France*; C. Gilles, E. Despiau-Pujo,* LTM/CNRS-UGA, France

Image sensors used in smartphones have seen a lot of technological development over the past decade aiming pixel size reduction to improve photography resolution. One of the main component of these image sensors are microlenses, which focus the light incident on the photodiode, thus improving the quantum efficiency of the sensor. The manufacture of resist microlenses necessitates an etching step in a fluorocarbon plasma, during which a semi-spherical resist pattern must be transferred into a subjacent resist layer. Due to the complex chemico-physical processes taking place during etching, it is difficult to predict the final 3D shape of the microlenses. Thus, a better understanding of the link between the process conditions, the plasma properties, and the final microlens shape can assist the development of such new technology.

In this paper, we propose to numerically investigate the influence of different tunable process parameters on the plasma properties and the fluxes incident on the wafer. The CF4 plasma is simulated using a 2D hybrid model (Hybrid Plasma Equipment Model) in a dual-frequency capacitively coupled plasma reactor. We first investigate the impact of pressure (10-100 mT), RF power (100-1500 W) and gaz flow (100-500 sccm) on plasma bulk properties such as the electron and ion densities, the radical composition and the electronic temperature. In agreement with experiments reported in literature, F, CF3, CF and CF2 are shown to be the main radicals in the plasma. Increasing the low-frequency (13,56 MHz) power increases the ion energy at the wafer, while increasing the high-frequency (40 MHz) power allows to control the plasma density and the ion flux at the wafer. The detailed impact of process parameters on the fluxes and energy distribution functions of species (radicals, ions) impacting the wafer will be discussed during the presentation.

12:00pm **PS2+MS-TuM-13 Investigation of N_2 Plasma in Plasma Enhanced Atomic Layer Deposition of Silicon Nitride Using First Principles Calculation***, **Tsung-Hsuan Yang**, T. Wang, G. Hwang,* University of Texas at Austin*; P. Ventzek, T. Iwao, J. Zhao,* Tokyo Electron America Inc.,*; K. Ishibashi,* Tokyo Electron Ltd., Japan

Plasma-enhanced atomic layer deposition (PEALD) has been demonstrated to be a promising technique for the controlled growth of silicon nitride (SiN) thin films. The benefits of PEALD include excellent conformality, precise thickness control, and high quality at relatively low temperatures (<400^{o}C). In this work, density functional theory (DFT) was applied to study the surface reaction mechanism when a Si-rich surface is exposed to N_2 plasma. The reactive species in N_2 plasma, atomic N, tends to react with a undercoordinated N or a tertiary amine by forming a N_2-dimer. After subtle surface reconstruction, three types of N_2-dimer (Si-N-N-Si, Si_2-N-N-Si_2, and Si_2-N-N-Si_2) were created, depending on the abundance of neighboring Si. These N_2-dimers were relatively stable and can remain after N2 plasma half cycle. The reactions between silane (SiH_4) and trisilylamine (TSA, $(SiH_3)_3N$) precursors and N_2-dimers were then examined and compared. Results show that one H from the Si precursor will first migrate to one N in the N_2-dimer, saturating the undercoordinated N and rendering a Si dangling bond in the precursor. The other N in the N_2-dimer will then initiate a nucleophilic attack toward the Si dangling bond in the precursor and forms a Si-N bond. Meanwhile, the N-N in the N_2-dimer is broken. The whole reaction is highly exothermic due to the destruction of weak N-N single bond and formation of strong Si-N bond. Most importantly, the Si precursor remains intact during the reaction, indicating that using a bulkier precursor with three silyl ligands such as TSA can guarantee a higher growth rate rather than silane. These findings agree well with previous experimental results.

Surface Science Division
Room 319 - Session SS-TuM
Liquid/Solid Interfaces and Electrochemistry

Moderators: Kathryn Perrine, Michigan Technological University, **Michelle Personick**, Wesleyan University

8:00am **SS-TuM-1 Investigating the Oxidation of Pt(111) Using High-Pressure Scanning Tunneling Microscopy, Force Field Calculations, and Ab Inito Thermodynamics***, D. Boden,* Leiden University, Netherlands*; M. van Spronsen,* Diamond Light Source, UK*; J. Frenken,* ARCNL*; J. Meyer, **Irene Groot**,* Leiden University, Netherlands

Platinum has always been an important catalyst for oxidation reactions in the automotive industry, but also for electrocatalysis. Therefore, oxidation of and on platinum surfaces has long been a favorite topic in the field of surface science.Recently, the development of in situ and operando techniques has shown that the classic ultrahigh vacuum (UHV) approach is inadequate to describe the catalyst at realistic catalytic conditions. We will show that under these conditions (>530 K and>1 bar O_2), the Pt(111) surface oxidizes and forms spoke wheel and stripe-like structures that are not stable under UHV conditions. The striped structures we found using high-pressure scanning tunneling microscopyhave since been investigated using a combination of density functional theory (DFT) and ab initio thermodynamics (AITD) to evaluate the surface free energy at realistic temperatures and pressures. Here we do the same for the spoke wheel structure. However, since even the smallest candidate structures are too large for ordinary DFT calculations, we employ a ReaxFF force field developed specifically for Pt and O. This force field is able to accurately reproduce results from DFT and allows us to obtain an atomic model for the spoke wheel structure that matches the experimental results closely. Using AITD we compare its relative stability to the stripe structures over a large range of temperatures and pressures. We show that the spoke wheel structure is more stable than the stripe structure if the surface is partially oxidized, while the stripe structure is more stable only if it covers the entire surface.

8:20am **SS-TuM-2 Operando Electrochemistry: NAP-XPS on Electrolyte/Electrode Interfaces - Studies of Liquid Electrolytes and Their Interfaces to Battery Cathodes for Lithium Ion Battery Applications***, **Francesca Mirabella**, P. Dietrich, A. Thissen,* SPECS Surface Nano Analysis GmbH, Germany

In this work, we present NAP-XPS results from model and commercial liquid electrolytes for lithium-ion battery production using an automated laboratory NAP-XPS system. As electrolyte solutions, we used LiPF6 in EC/DMC (LP30) as a typical commercial battery electrolyte and LiTFSI in PC as a model electrolyte. We analyzed the LP30 electrolyte solution, first in its vapor and liquid phase to compare individual core-level spectra. In a second step, we immersed a V_2O_5 single crystal as a model cathode material in this $LiPF_6$ solution. Additionally, the LiTFSI electrolyte model system was studied to compare and verify our findings with previous NAP-XPS data. Photoelectron spectra recorded at pressures of 2–10 mbar show significant chemical differences for the different lithium-based electrolytes.

8:40am **SS-TuM-3 AVS Dorothy M. and Earl S. Hoffman Scholarship Talk: Infrared Nanospectroscopy for Solid-Liquid Interface***, **Xiao Zhao**[1,2], M. Salmeron,* LBNL

Nanoscale properties and dynamical processes at solid-liquid interface are critical for many natural phenomenon and industrial applications, including energy storage, self-assembly and corrosion. However, fundamental study of those processes is often challenged by radiation damage from electron or X-ray probe, which may drive the structure and chemical states of interface away from its original state. Herein we demonstrate a new non-destructive platform that enables nanoscale interfacial sensitive Infrared (IR) spectroscopy for solid-liquid interface by combining graphene liquid cell and Fourier Transform Infrared Nanospectroscopy (nano-FTIR). With that we investigated the nanoscale structural evolution and response of protein assemblies to external environments as well as dynamical interaction between nanoparticles with ligand capping layer for CO_2 electroreduction. The protein substructure and ordering, and specific adsorption configuration of ligand on nanoparticles are monitored by their characteristic IR vibrational bands at nanometer scale under realistic condition, which provides complimentary information to other operando techniques. Our platform opens broad opportunities for *operando* study of soft materials or nanostructures (membrane protein, virus, nanoparticles and plastic material) in their realistic condition and under external stimuli.

9:00am **SS-TuM-4 Methods for Exposing UHV-prepared Metal Oxide Surfaces to Liquid Water: A Comparison of TiO_2, Fe_2O_3, and Fe_3O_4***, **Jiri Pavelec**, J. Balajka, F. Kraushofer,* Vienna University of Technology, Austria*; Z. Jakub,* CEITEC, Czechia*; G. Franceschi, M. Schmid, G. Parkinson, U. Diebold,* Vienna University of Technology, Austria

The importance of bridging the pressure gap in studies of model catalysts has been recognized for decades. The investigation of surfaces under ambient conditions remains a challenge due to the restricted number of experimental techniques available and a high risk of contamination. The design of two working instruments for tackling the pressure gap in surface science will be presented: An apparatus for dosing liquid water in an ultrahigh vacuum [1,2] and a high-pressure cell [4]. The first instrument allows dosing a droplet of ultrapure liquid water on the surface of a sample without exposure to air. The second presented instrument is a novel design of a high-pressure cell, intended to expose metal-oxide single crystals to water vapour pressure up to the mbar range and elevated temperatures. Both instruments are coupled to an existing surface-science chamber, enabling reproducible sample preparation and sample characterization using UHV-based analytical techniques (q+AFM, XPS, LEIS). By exposing a number of metal oxides to liquid water we have learned that some surfaces stay intact, some are slightly modified, while some are completely changed. For example, no change is found after water drops or vapour exposure to rutile $TiO_2(110)$ [2], and it can be utilised as a benchmark system for clean liquid water dosing. The α-$Fe_2O_3(1\bar{1}02)$ surface exchanges oxygen with vapor and liquid water, but retains the UHV structure [3]. A more significant change was observed for $Fe_3O_4(001)$: Multi-Langmuir water doses do not change a $(\sqrt{2} \times \sqrt{2})R45°$ reconstruction under UHV conditions, but liquid water at room temperature lifts the reconstruction [4] followed by the formation of a partial oxyhydroxide layer.

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9:20am **SS-TuM-5 Interplay of Structure, Dynamics and Energetics of Alkali Metal Ions on Muscovite Mica Surfaces: Molecular Dynamics Simulation***, **Alper T. Celebi**,* Vienna University of Technology, Austria*; S. Reindl,* Friedrich-Alexander-Universität Erlangen-Nürnberg, Germany*; M. Olgiati,* Vienna University of Technology, Austria*; T. Bauer,* Friedrich-Alexander-Universität Erlangen-Nürnberg, Germany*; L. Maers, M. Valtiner,* Vienna University of Technology, Austria

Adsorption of ions at the solid-liquid interface is of great importance in various physical processes such as corrosion of metals, electrochemical energy storage, swelling of clays, biofouling in the marine environment and transport in shale rocks. In these processes, the type of cation in an electrolyte solution has a profound influence on the hydration structure, dynamics and energetics of the ions at the interface. Atomistic simulations are practical to properly explore such influences at the molecular resolution. In this study, we performed molecular dynamics (MD) simulations of different aqueous salt electrolytes confined between two negatively charged mica surfaces. As the electrolyte, we used chlorides of different alkali metals, namely Cs^+, K^+, and Li^+. We explored the variations in interfacial water density, ion concentrations, structural orientations, ion mobilities and hydration energies. Our simulations show that Cs^+ has prominent concentration peaks at the surface, indicating very strong ion adsorption. Unorthodoxly, there are more counter-charges at the interface than is on the mica surface, which result in non-classical charge overscreening. However, this is not the case for Li^+ ions. They bound less strongly to the surface. Thus, Li^+ concentrations at the interface are lower than for Cs^+ and K^+ at the same molar concentration. This behavior is further supported by the ion mobilities at the interface where Cs^+ ions are found to be more stagnant while Li^+ ions are more mobile and K^+ ions have intermediate characteristics. Another interesting finding is that Cs^+ and K^+ ions predominantly sit at the cavity center of muscovite mica, creating a diamond-shape pattern. On the contrary, Li^+ cations are located on the charged oxygen site of the mica with slit-like formation. We asses that such structural orientations are mainly due to the differences in the ion sizes and electron densities. Moreover, water densities for Li^+ solution show the most pronounced oscillatory layering at the interface. Although there are less Li^+ ions at the surface compared to K^+ and Cs^+,more water molecules come near to the surface depleting the center of the channel for Li^+ case. This clearly points out that hydration forces are more effective for the aqueous Li^+ solution while the surface and metal ion interactions are the driving forces of Cs^+ and K^+ solutions. We also found out that the effect of the molar concentration has a negligible role on structure and energetics of mica and electrolyte interfaces. High-resolution atomic force microscopy imaging is being performed in parallel to further support our MD simulations.

9:40am **SS-TuM-6 Corrosion Mechanism of Aluminum Alloy at Grain Boundaries Investigated by in-Liquid Nanoscale Potential Measurement Technique***, **Shinnosuke Yamamoto**, D. Taniguchi, T. Okamoto, K. Hirata,* Kanazawa University, Japan*; T. Ozawa,* Kobe Steel, Ltd., Japan*; T. Fukuma,* Kanazawa University, Japan

Al-Zn-Mg alloys are used as a structural material for automobiles and aircraft due to their outstanding strength. However, the high susceptibility to the local corrosion and stress corrosion cracking of the Al-Zn-Mg alloys limits their applications. The high susceptibility of Al-Zn-Mg alloy to the local corrosion is caused by the microstructural inhomogeneities such as the grain boundaries (GBs) and intermetallic particles. Along GBs of these alloys, a line-shaped precipitate free zone (PFZ) made of aluminum is formed. In addition, inside the PFZ, granular precipitates made of $MgZn_2$ are distributed along the GBs. The coexistence of these different materials forms corrosion cells to induce corrosion at the GBs. However, nanoscale mechanisms of such corrosion have been elusive. To solve this problem, we have directly imaged the corrosion behavior near the GBs of Al-Zn-Mg alloys in liquid on a nanoscale using a local potential measurement technique referred to as open-loop potential microscope (OL-EPM) (Fig.1).We imaged the changes in topography and potential at the same location during and after replacing the solution from water to pH 2.2 H_2SO_4 solution by OL-EPM. At 28 min after the immersion of an Al-Zn-Mg alloy sample, high potential spots were observed inside the GBs (Fig. 2 (a) and (b), red arrows), which probably correspond to the $MgZn_2$ precipitates. Meanwhile, the relatively low potential area around $MgZn_2$ precipitates should correspond to the PFZ (Fig.2 (a) dotted line). Previous studies showed that the high potential area has high corrosion activity. Thus, the observed high potential areas suggest the anodic dissolution of the $MgZn_2$ precipitates. Indeed, the height profiles measured across one of the precipitates reveal a 10 nm height decrease caused by replacing water with

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[1] **SSD Morton S. Traum Award Finalist**

[2] **AVS Dorothy M. and Earl S. Hoffman Scholarship Recipient**

the H_2SO_4 solution (Fig.2 (c)). At 97 min, the bright spot was not observed at the GB (Fig.2 (b) (iii)). This disappearance suggests the complete dissolution of the $MgZn_2$ precipitate. Consequently, the PFZ area shows a lower potential than the surrounding matrix. In addition, small anodic and cathodic regions are formed all over the matrix, forming many local corrosion cells. The dissolution of these anodic areas increased the surface roughness as confirmed in the height profile shown in Fig.2 (c). Based on these observations, we found that the $MgZn_2$ and PFZ areas respectively serve as the anode and cathode in the initial stage of the corrosion at GBs. After the complete dissolution of $MgZn_2$ precipitates, the matrix starts to serve as an anode instead of the $MgZn_2$ precipitates.

11:00am **SS-TuM-10 Identifying Available Adsorption Sites on Au-Ps Alloys by FTIR Spectroscopy and Monte Carlo Simulations***, S. Manzi,* Dep. de Física, Universidad Nacional de San Luis, Instituto de Física Aplicada, CONICET, Argentina*; M. Bosco, M. Brites Helú,* Instituto de Desarrollo Tecnológico para la Industria Química (INTEC), UNL/CONICET, Argentina*; A. Baldo,* Fac. de Ingeniería Química (FIQ), Universidad Nacional del Litoral (UNL), Argentina*; S. Collins, **Florencia Calaza**,* Instituto de Desarrollo Tecnológico para la Industria Química (INTEC), UNL/CONICET, Argentina

Available adsorption sites on the surface of bimetallic AuPd compounds were studied by comparison of experimental results of CO adsorption, used commonly as a probe site molecule, on catalysts (powders) AuPd/CZ (ceria-zirconia) prepared in a relation 1:1 (Au:Pd), and on catalyst model surfaces prepared over single crystals. On both systems the sites exposed for CO adsorption are modified by calcining or heating the material to specific temperatures, allowing surface and bulk Au and Pd reordering. The spectroscopy results from both systems present some degree of agreement supporting in this way the need for interdisciplinary research to study catalytic systems. Furthermore, the system was also characterized by Monte Carlo simulations, which give an explanation for the increased availability of Pd atop sites experimentally observed, by forming Pd chains across the surface and avoiding 3-fold site formation due to agglomeration of Pd atoms.

11:20am **SS-TuM-11 Role of Chemisorbing Species in Growth at Liquid Metal-Electrolyte Interfaces Revealed by in Situ X Ray Scattering***, **Andrea Sartori**,* ESRF, France

Liquid-liquid interfaces offer intriguing possibilities for nanomaterials growth. Especially, growth at liquid metal surfaces has recently received renewed interest. Here, fundamental interface-related mechanisms that control the growth behavior in these systems are studied for the case of Pb halide compound formation at the interface between liquid mercury electrode and aqueous salt solutions, using in situ X-ray reflectivity and grazing incidence X-ray diffraction, supplemented by electrochemical measurements and optical microscopy. The nucleation and growth of these compounds at potentials in the regime of Pb de-amalgamation was investigated in NaX + PbX_2 (X = F, Cl, Br) to systematically explore the role of the halide species. X-ray reflectivity studies reveal the rapid formation of well-defined ultrathin precursor adlayers in Cl- and Br-containing solution. This adlayer formation is followed by subsequent quasi-epitaxial growth of Pb(OH)X bulk crystals, that are oriented with the c-axis along the surface normal. In contrast, growth in F-containing solution proceeds by slow formation of a more disordered deposit, resulting in random bulk crystal orientations on the Hg surface. A detailed structural analysis of the Pb(OH)Br and Pb(OH)Cl precursor adlayers reveals that they determine the orientation of the subsequently formed bulk crystals, with the arrangement in the adlayer providing a template. Together with our previous results on the pseudo-epitaxial growth of PbFBr on Hg (A. Elsen, et al., Proc.Nat.Acad.Sci., 2013, 110, 6663), these data reveal the decisive role of the interface chemistry, especially the strong chemisorption of the anions bromide and chloride, in steering the formation of these textured deposits at the liquid metal surface.

11:40am **SS-TuM-12 In Situ Electrochemical STM Imaging of an Au Electrode Identifying the Active Sites during the Electrocatalytic Process***, **Yongman Kim**,* Korea Advanced Institute of Science and Technology (KAIST) & Institute for Basic Science (IBS), Republic of Korea*; Y. Jeong,* Institute for Basic Science (IBS), Republic of Korea*; Y. Kim, J. Park,* Korea Advanced Institute of Science and Technology (KAIST) & Institute for Basic Science (IBS), Republic of Korea

Understanding the influence of surface structural features is important for guiding mechanistic proposals for electrocatalytic reactions of the electrode. However, atomistic knowledge of the actual active sites remains elusive, because of the complicated relationship between structural stability and catalytic activity. With this in mind, we have focused on the fundamentals of the electrocatalytic process, using in situ electrochemical STM, and on locating the real active sites, a longstanding issue. In this work, we present STM results on two-dimensionally well-ordered manganese porphyrin structures on Au(111). We show that manganese porphyrins are oxidized after water oxidation and promptly decompose into catalytically active species as bright protrusions. These newly formed active species have dramatically lost their catalytic activity, either by acid treatment, one of the oxide removal methods, or by deposition of phosphonic acid, one of the oxide–favoring materials. This confirms that the active species are composed mainly of manganese oxides as a water oxidation catalyst. We extended our study to examine the surface structural sensitivity of Au single crystals itself for electrocatalytic CO_2 reduction as a simple model study. As the most active electrocatalyst for CO_2 conversion into CO, Au(*hkl*) shows structural dependency on coordinated sites, such as the terrace of Au(111) and the steps of Au(332). Through real-time electrochemical STM measurements, we have confirmed that these are the actual active sites for CO_2 reduction. A remarkable finding of our work provides the molecular evidence for Au and modified-Au electrode's active sites, providing impetus for future application in water oxidation and CO_2 reduction catalysts, as the data establishes a relationship between catalytic activity and structural changes.

12:00pm **SS-TuM-13 Extreme Atomic-Scale Surface Roughening: Amino Acids on Ag on Au(111)***, E. Cook, K. P.S. Boyd, M. Paszkowiak, **Erin Iski**,* The University of Tulsa

A clear description of how surface morphology is affected by the bonding of biomolecules, like amino acids, with metal surfaces is critical to identify due to the potential applications in microelectronics, medical devices, and biosensors. Amino acids (AAs) on clean Au(111) were previously observed to trap Au adatoms, eventually leading to the formation of one atom high metal islands whose area was related to the amino acid molecular weight. To better understand the role of surface identity, L-Isoleucine on Au(111) modified with a Ag thin film was investigated at ambient conditions with Electrochemical Scanning Tunneling Microscopy (EC-STM). The atomically-thin Ag films were deposited on the Au(111) using Underpotential Deposition. The mere presence of a Ag monolayer drastically changed the amino acid/surface interactions despite the chemical similarity of Au and Ag. The adsorption of the AAs on the Ag monolayer drastically altered the surface and caused significant surface roughening distinct from 2D growth which had previously existed only on top of the surface. This roughening occurred layer-by-layer and was not restricted to the first layer of the surface as seen with sulfur containing molecules. Notably, this study demonstrates surface roughening that is occurring under extremely mild conditions highlighting the ability of Ag thin films to markedly alter surface chemistry in concert with biomolecules.

Thin Films Division
Room 316 - Session TF-TuM

Growth in 3D, High Aspect Ratio and Nanostructured Materials

Moderators: Adriana Creatore, Eindhoven University of Technology, Netherlands, **Richard Vanfleet**, Brigham Young University

8:00am **TF-TuM-1 Tailoring 3-D Nanomaterial Architectures Using ALD: Bridging Scales from Atoms to Bulk***, **Neil Dasgupta**,* University of Michigan **INVITED**

As we move towards a vision of "materials by design" in the 21st century, the ability to rationally control hierarchical material architectures becomes increasingly critical. This is inspired by natural systems, which routinely achieve material properties that are not available in the bulk through precise ordering across several orders-of-magnitude in length scale. However, while there have been tremendous advances in self-assembly and additive manufacturing in three dimensions to create periodic structures such as meta-materials, as we move towards composite material architectures composed of multiple dissimilar materials, heterogeneous interfaces play an increasingly important role. In particular, integration of materials with significantly different mechanical, thermal, optical, and/or electronic properties into "bulk" hierarchical architectures requires atomically-precise and deterministic control of surfaces and interfaces.

In this talk, I will demonstrate examples of how Atomic Layer Deposition (ALD) is a key enabling technique to enable the rational design of hierarchical material systems. These atomically-precise surface modifications can be used to direct self-assembly processes, provide tunability of the optical, electronic, thermal, and mass transport properties of integrated material systems, and encapsulate structures to promote their stability in a wide range of environments. I will present examples of how ALD can enable hierarchically-structured materials by design, including three-dimensional solid-state batteries, photocatalysts for solar fuel conversion, multi-functional composites, and anti-fouling surfaces. I will further provide a perspective on how this versatile approach can lead to the design and scaled-up manufacturing of material systems with precision at length scales ranging from atoms to meters

8:40am **TF-TuM-3 Thin Film Technology and Diagnostics for Multilayered Solid-State Batteries*, Victoria Castagna Ferrari*,** *G. Rubloff, D. Stewart,* University of Maryland, College Park

Thin-film solid-state batteries (SSBs) can provide high-power performance with easy miniaturization and on-chip integration, but broader applications demand higher energy density. Thin film fabrication enables new cell architectures to achieve this. Using sequences of in-situ patterning and deposition, we were able to produce a multilayered battery in a 3D architecture like a prismatic pouch cell. The advantages of such unique design are: i) individual solid-state batteries can be small (µm to cm scale) and shaped to fit the application while providing faster charge and discharge; ii) a multilayered stack, where the cathode and anode layers are connected on either sides in parallel, minimizes passive structural material, thereby improving the total device energy density; and iii) applying multilayer shadow masking during sputtering avoids high-aspect ratio deposition challenges.

Prototypes of this prismatic battery with 1 and 3 layers were made using the sputtering tool to judge the scaling of discharge capacity and power performance. Thin films of silicon, LiPON, and lithiated vanadium oxide (LVO) were deposited as the anode, electrolyte, and cathode layers to produce a battery with tunable lithium content, without breaking vacuum during the entire fabrication sequence. As a final step, the whole SSB stack was post-annealed at 300 °C. A single-layer prototype device with area 0.15 cm^2 and total battery thickness 1µm was electrochemically active when cycled between 0 and 4 V. Charge-discharge testing showed an initial capacity of 50 mAh/g under fast rate (5C) with a Coulombic efficiency of 98 %.

Our initial multibattery device, comprising a three-battery stack, revealed rougher interfaces and susceptibility to delamination. SEM-cross-sectional images showed unexpected voids in the LVO/LiPON interface, suggesting side reactions and possible additional lithiation of the LVO from the LiPON layer. Clearly, understanding and controlling interfaces will be crucial to multilayered thin-film batteries. Hence, we have conceived a new diagnostic platform for developing multilayer SSBs comprised of new shadow masks configured to characterize properties of each active layer and interface, as well as the entire multibattery device, using electrochemical impedance spectroscopy (EIS) and equivalent circuit modeling of the full battery and its constituent components. As a preliminary result, we found that the LVO/LiPON interface represents the largest contribution to the total cell impedance. As simultaneous high power and high energy drive multibattery SSB architectures, revealing properties of individual interfaces and layers will be crucial to success.

9:00am **TF-TuM-4 Interface Mixing in Thin-Film Solid-State Sodium Batteries*, Blake Nuwayhid,*** *A. Kozen,* University of Maryland*; D. Long,* Air Force Research Laboratory, USA*; G. Rubloff, K. Gregorczyk,* University of Maryland

Nanostructured solid-state batteries (SSBs) are poised to meet the demands of next-generation energy storage technologies, with atomic layer deposition (ALD) being a powerful tool enabling high-performance nanostructured SSBs that offer competitive performance with their liquid-based counterparts. Furthermore, switching from lithium-ion batteries to those based on the more abundant sodium-ion charge carrier is an attractive route to decrease costs. Recently, we developed an ALD process for sodium phosphorus oxynitride (NaPON) as a solid-state sodium ion electrolyte.[1] NaPON proved to be an effective solid-state electrolyte (SSE) with an ionic conductivity of 1.0 x 10^{-7} S/cm at 25 °C and a wide electrochemical stability window of 0-6.0 V vs. Na/Na^+. In this presentation, thin-film solid-state sodium batteries are explored, in which NaPON is paired with a V_2O_5 cathode and a thermally evaporated Na metal anode. Electrochemical analysis of the SSB suggests intermixing of the NaPON/V_2O_5 layers during fabrication. We investigate this interfacial reactivity in three ways: with *in-situ* spectroscopic ellipsometry, time-resolved XPS depth profiling, and cross-sectional cryo-TEM. We characterize this reaction during the ALD NaPON deposition on V_2O_5 to be two-fold: (1) reduction of V_2O_5 to VO_2 and (2) Na^+ insertion into VO_2 to form Na_xVO_2. The Na metal evaporation process is found to intensify this reaction, resulting in the formation of irreversible interphases between discrete battery layers. Despite the mixed interphases formed during fabrication, the SSB can operate for over 100 cycles and represents the first demonstration of a functional thin-film solid-state sodium-ion battery. This work highlights the high reactivity of Na compared to Li-based battery chemistries, not only necessitating the need for interfacial coatings in Na-SSBs, but also helps to define design rules required during fabrication of Na-SSBs or liquid Na-ion batteries.

32. Nuwayhid, R. B.; Jarry, A.; Rubloff, G. W.; Gregorczyk, K. E., Atomic Layer Deposition of Sodium Phosphorus Oxynitride: A Conformal Solid-State Sodium-Ion Conductor. *ACS Applied Materials & Interfaces* **2020,***12* (19), 21641-21650.

9:20am **TF-TuM-5 Direct CVD Synthesis of MgH_2 Thin Films and Nanowires by Decomposition of the Novel Magnesium *Bis*-Diamidodiboranate Precursor*, Laurent Souqui*,** *C. Caroff, S. Shrivastav, G. Girolami, J. Abelson,* University of Illinois at Urbana-Champaign

MgH_2 is a wide-bandgap light-weight dielectric which can be fully dehydrogenized to form metallic Mg above 410 °C. For these reasons, it has been extensively studied as a potential material for switchable windows and for hydrogen storage and fuel cells, and as a passivation layer for Si-based photovoltaic devices. Compared to common synthesis routes to MgH_2, such as high energy ball milling and liquid phase nanoconfinement, chemical vapor deposition (CVD) allows reduced synthesis time and process scalability with precise control of grain size and distribution to afford ultrathin layers. Unlike sputtering and evaporation, CVD is not a line-of-sight technique; at low deposition temperature, limited precursor reactivity produces highly conformal deposition on complex morphologies and structures. In the present work, a new CVD precursor, magnesium *bis*-diamidodiboranate ($Mg[N(Me)_2\text{-}BH_2\text{-}N(Me)_2\text{-}BH_3]_2$, $Mg(NBNB)_2$), was designed for clean reactivity at low temperatures. We report the direct synthesis of α-MgH_2 thin films by CVD from $Mg(NBNB)_2$ in the range 80-350 °C and 10-60 mTorr, affording growth rates of 1.9 to 11.3 nm/min. In contrast with earlier works, which utilized the composition of the gas phase to infer the synthesis of MgH_2 from alkyl magnesium precursors, we document the formation of MgH_2 using thin film characterization techniques.

We found that only the mass-transport-limited regime could be accessed even at the lowest deposition temperature, indicating that the reaction sequence of the precursor with the growing MgH_2 surface has relatively low energy barriers. This is in contrast with the interaction of the precursor with the substrate surface, as a significant nucleation delay was observed, lasting from 7 min at 170 °C to 20 min at 350 °C. We suggest that this delay is due to an increasing desorption rate of the precursor, an increasing instability of initial nuclei or an increasing diffusion rate of Mg into the substrate. The crystallinity of the films was found to be independent of the temperature and was mostly affected by the precursor partial pressure. Above 170 °C the morphology of the films changes from granular to a percolated network of islands and nanowires grew extensively above 200 °C. These nanowires were found to be 50 nm in diameter, which makes them interesting for application in hydrogen storage. The refractive index and absorption coefficient were found to be dependent both on deposition pressure and deposition temperature, this behavior is attributed to the tendency of MgH_2 to form H vacancies at high vacuum and high temperature conditions.

9:40am **TF-TuM-6 The Fabrication of Heterojunctions by Atomic Layer Deposition for Gas Sensing Applications*, Nicola Pinna,*** *H. Raza,* Humboldt University Berlin, Germany

Material and methods for detecting a wide range of harmful species are becoming increasingly necessary as automation and industrial growth increase. Chemoresistive gas sensors using semiconducting metal oxides (SMOX) are fundamental for developing efficient gas sensors. The sensitivity and selectivity of these nanostructured SMOX can be boosted by combining them with other SMOX. Yet control over the thickness of the shell layer is crucial; particularly, a thin shell layer modulates the space charge layer at the interface, thereby influencing effectively the charge conduction channel. The engineering of heterojunctions with well-defined core and shell layers is required to better understand the sensing response of heterostructured nanomaterials. A comprehensive understanding of the role of semiconductor heterojunctions and the sensing response of core-shell heterostructures is achieved by synthesizing a series of well-defined and well-controlled heterostructures with varying core and shell layers. NiO- and SnO_2-based hierarchical coaxial core-shell heterostructures are therefore proposed to achieve this objective. The designed heterostructures exhibit sensing responses related to the NiO or SnO_2-shell layers, or in some cases to the heterojunctions between $_n$SMOX (SnO_2) and $_p$SMOX (NiO). A comparison of the sensing response in order to understand the transduction mechanism across the interfaces in atomic layer deposition grown heterojunctions will be presented.

11:00am **TF-TuM-10 Tunable ALD Infiltration into High-Aspect-Ratio Aerogels Enabled by Process Modeling for Solar Thermal Applications***, Andrew J. Gayle*[1]*, Z. Berquist, Y. Chen, A. Davoodabadi, A. Hill, J. Hoffman, A. Bielinski, A. Lenert, N. Dasgupta,* University of Michigan, Ann Arbor

ALD provides a unique opportunity to impart conformal surface functionalization onto ultra-high-aspect-ratio structures, but depositions are complicated by precursor diffusion and dosing limitations. ALD modifications on substrates such as aerogels help enable their use in fields such as concentrated solar thermal (CST), catalysis, and filtration. SiO_2 aerogels possess a unique combination of desirable properties for CST applications, including high optical transparency and low thermal conductivity, but they suffer from poor stability at elevated temperatures. In this work, we investigate the ALD conditions needed to conformally modify SiO_2 aerogel monoliths (AMs) with aspect ratios >60,000:1 [1]. To minimize precursor waste during the long diffusion times necessary to conformally modify the AMs, we implemented a multi-dose-quasi-static-mode (multi-dose-QSM) deposition procedure. In standard QSM recipes, reactor pumping is halted during an "exposure step", allowing precursor to diffuse into a structure without being purged. In the multi-dose-QSM technique, multiple doses and exposure steps of a single precursor are implemented prior to dosing the counter reactant. This was necessary due to the large surface area of the AMs.

To enable tunable ALD infiltration depths into the AMs, we developed a model of the multi-dose-QSM deposition process. Our model accounts for precursor depletion in the ALD chamber during an exposure step and the effect of multiple precursor doses. This model also allowed for the optimization of the ALD modification process, including precursor usage efficiency and total process time.

SEM-EDS was used to quantify the ALD infiltration depth to validate the model. ALD saturation was further confirmed using mass gain measurements. The ALD-modified AM also showed improved resistance to structural degradation at elevated temperatures, likely due to stabilization of the SiO_2 nanoparticles. These changes may be due to the formation of a ternary Al-Si-O phase at the interface between the SiO_2 backbone and Al_2O_3-based modification, as shown using XPS measurements. This leads to an improved retention of the low thermal conductivity and high transmittance following annealing, compared to bare SiO_2 AMs. This combination of properties makes the ALD-modified AMs a promising transparent insulating material for CST applications [2]. ALD-modified AM synthesis is currently being scaled up from ~25.4 mm-diameter discs to ~155 x 65 mm tiles for use in a prototype CST receiver.

[1] A. J. Gayle, Z. J. Berquist et al. *Chem. Mater.* **2021**, *33* (14), 5572-5583.

[2] Z. J. Berquist, A. J. Gayle et al. *Adv. Func. Mater.* **2022**, 32 (12), 2108774.

11:20am **TF-TuM-11 Ultra-thin, Conformal ALD Films for Reliable Corrosion Resistance in SLM Metal Additive Manufactured Surfaces***, **Timothy J. Gorey**,* Los Alamos National Laboratory

Metal additive manufacturing (MAM) is a valuable method for prototyping and circumventing the geometry constraints of conventional manufacturing methods, such as machining or extrusion. The field of MAM is still relatively novel, and aging properties, such as unpredictable corrosion resistance, hinder widespread application and reliable interchangeability with traditionally manufactured parts. Here, we utilize the self-limiting deposition method of atomic layer deposition (ALD) to apply ultra-thin, conformal anti-corrosion barriers onto monolithic 316L stainless steel surfaces. Substantial improvement in corrosion reliability was repeatedly obtained on single-surface, proof-of-concept coupon samples for thicknesses ranging from a few to hundreds of nanometers. This presentation will discuss the unique advantages and nuances of ALD and its relevance to MAM components. Corrosion results for coated and uncoated MAM 316L surfaces will also be discussed that predict ALD to be a viable post-manufacturing approach in MAM parts.

11:40am **TF-TuM-12 Atomic Layer Deposition of Superconducting Films for Through-Silicon-Via Structures and Photon Detection***, **John Femi-Oyetoro**, H. LeDuc, P. Day, F. Greer,* Jet Propulsion Laboratory (NASA/JPL)

Superconductors traverse to normal metal behavior in the millimeter-far-IR wavelength range as consistently described in the Bardeen-Cooper-Schrieffer (BCS) theory. This property has been explored and leveraged upon in Astrophysics, for detecting the early universe in the millimeter-far-IR spectrum, where radiation appears to be the strongest. The first light emitted after the Big Bang approximately 14 billion years ago can still be detected as the cosmic microwave background (CMB), and superconductors have aided this effort. Superconducting (SC) detectors are essential and have scientific opportunities in solving key problems in astronomy and cosmology. To buttress, at Jet Propulsion Laboratory, SC transition edge sensors have been deployed at the South Pole, including the Background Imaging of Cosmic Extragalactic Polarization (BICEP) telescopes and the Keck Array. These instruments have performed CMB polarization measurements with great sensitivity to the signatures of the early universe. In addition, kinetic inductance SC detectors are been utilized in future missions and concepts such as the Terahertz Intensity Mapper (TIM) balloon experiment and Galaxy Evolution Probe (GEP) for integral field spectroscopy. In this work, we demonstrate the deposition of high-quality SC films such as titanium nitride (TiN) with high transition temperature and kinetic inductance for high-density through-silicon-via (TSV) structures for large photon detectors arrays. SC films provides outstanding sensitivity, mature fabrication, and large array sizes, for multiplexing and hybridization techniques. However, while conventional sputtering technique have been useful in fabricating SC detectors, atomic layer deposition (ALD) has provided an advantage of spatial uniformity and conformality. These properties are absent in sputtering techniques. We employed ALD to control the repeatability, composition and thickness, which plays a role in the transition temperature of SC films. These possibilities have an advantage to explore different SC materials for specific detection application in future science observations. We also explored different precursors and deposition conditions, including temperatures as low as 200 °C. In a nutshell, we are interested in TSV SC films with spatial uniformity, high-aspect-ratio and high transition temperature, that will overcome the challenges of interconnect density using 3D integration. We believe that, extending these integration techniques to SC detectors are very crucial in the 3D hybridization of high-density pixel detector arrays with outstanding sensitivity. Results aiding these TSV structures for SC detectors will be discussed.

12:00pm **TF-TuM-13 Reliable RF and DC Plasma-Power Solutions Supporting Today's Demanding Industrial Applications***, **Mike Meyer**, P. Maloney,* Advanced Energy Industries, Inc., USA

Process stability, reliability, and repeatability are key to optimizing yield in advanced plasma-based applications. As these processes become more complex, involving numerous steps and rapid plasma transitions, accurate control of the power to ignite, maintain, and manipulate the plasma becomes increasingly critical. This presentation describes developments in RF and DC power-delivery technologies and techniques that enable these demanding manufacturing applications, including bipolar DC pulsing with customizable waveforms, and RF-power phase synchronization, real-time impedance management, customizable arc management, and waveform controls. It also explains how real-time access to power-delivery data and analysis provides intelligence that engineers and operators can apply immediately to refine process performance, as well as to predict and perform maintenance. Ultimately, combining the described power hardware with these critical insights can maximize yield and minimize downtime – crucial capabilities for today's semiconductor, glass, FPD, solar, and industrial applications.

Presenters:

Mike Meyer is a senior product manager at Advanced Energy with 23 years of experience in the precision thin-film industry, including eight years with RF and DC power systems for PVD, PECVD, and a variety of industrial, plasma-based, thin-film deposition applications. He also spent 15 years in the precision optical-coating industry specializing in ion-beam sputtering technology and complete optical coating system solutions.

Paul Maloney has four years of experience in the precision thin-film industry working with Advanced Energy plasma power products. He currently leads the DC Product Management team and is developing next-generation DC and pulsed-DC power supplies. He previously worked in the

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[1] **TFD James Harper Award Finalist**

defense industry and has an educational background in nuclear engineering.

Vacuum Technology Division
Room 301 - Session VT-TuM

Vacuum Technology for Large Vacuum Systems

Moderators: Chandra Romel, Consultant, **Marcy Stutzman**, Jefferson Lab

8:00am **VT-TuM-1 Vacuum Materials for the Next Generation Gravitational Wave Detectors*, Ivo Wevers*, *G. Bregliozzi, P. Chiggiato, M. Rimoldi, C. Scarcia, M. Taborelli,* CERN, Switzerland **INVITED**

Gravitational waves were detected for the first time in 2015 by the LIGO which, since then, has measured several other events in conjunction with VIRGO. These achievements have stimulated studies for next-generation gravitational telescopes to enlarge the discovery potential of such scientific facilities. Two studies are presently considered: the Cosmic Explorer (CE) and the Einstein Telescope (ET) in USA and Europe, respectively. To increase the detection performance a key parameter is the length of the Fabry-Perrot cavities in which high power laser beams are stored in an ultrahigh vacuum. For both CE and ET, more than 100 km of ~ Ø 1 m vacuum pipes are required, which would represent up to 50% of the total budget of the new experimental facilities if the LIGO and VIRGO’s configurations were adopted. To reduce the cost impact of the vacuum system, unconventional materials, less expensive pipe manufacturing and different surface treatments are scrutinized. In this work, we present measurements performed on low carbon steel (mild steel), having been proposed as an alternative to stainless steel. The outgassing rates of several as-cleaned low carbon steels were measured. Specific hydrogen outgassing rates at room temperature in the 10^{-15} mbar l s^{-1} cm^{-2} were measured for bakeout temperatures as low as 80°C for 48 hours. Water vapour outgassing rates of unbaked samples were similar to or higher than those of stainless steel. To reduce water vapour outgassing, so that a bakeout can be avoided, a silicon coating was proposed. The coating has been produced by chemical vapour deposition with silane as precursor gas; the resulting layer was several hundreds of nanometres thick and resulted in the reduction of the water vapour outgassing rate by a factor 10. Such a value is not low enough to eliminate the need of a bakeout but could open the possibility of temperature treatments below 100°C. Room-temperature specific hydrogen outgassing rates of the Si coated steels in the low 10^{-14} mbar l s^{-1} cm^{-2} were measured after bake-out at 80°C for 48 hours. The hydrogen intake in the studied steels during the coating was investigated by thermal desorption spectroscopy. Optimisation of the mild steel is under study in collaboration with industry to improve vacuum performance and corrosion resistance.

8:40am **VT-TuM-3 Vacuum Design for a Cryogenic Gravitational Wave Detector*, Rana Adhikari*, *C. Wipf,* California Institute of Technology **INVITED**

In 2016, the Laser Interferometer Gravitational-wave Observatory (LIGO) collaboration announced the first detection of gravitational waves (GWs) from the merger of black holes. These ripples in the fabric of spacetime are measured on the earth by laser interferometry. In order for these instruments to work, they must be able to measure mirror motions at the level of 10^{-21} m (100 billion times smaller than a hydrogen atom). The next generation of these instruments will be operated at cryogenic temperatures and use squeezed light to reduce the quantum measurement uncertainty. In this talk I will describe the limits to ultra-precision measurement and how the design of the vacuum system, cryogenic temperature, surface treatments, and laser wavelength affect the measurement. A successful vacuum design would enable the detection of exotic astrophysical phenomena from across the entire universe.

9:20am **VT-TuM-5 CSI; the New Space Calibration Facility at TNO*, Freek Molkenboer*, *R. Jansen,* TNO Science and Industry, the Netherlands*; W. van Werkhoven, T. Luijkx, W. Mulckhuyse,* tno Science and Industry, the Netherlands

In early 2018 TNO started with the conceptual design of a new Space calibration facility, called CSI. The CSI facility will be used for the performance verification and calibration of optical Earth observation instruments on satellites. before the summer of 2022 the facility will be installed and commissioned, and in Q4 2022 ready to receive customers.

CSI consists of a few major subsystems, a Thermal Vacuum Chamber (TVC), an instrument manipulation system (consisting of a hexapod and rotation table), a set of optical stimuli and an overall control system.

The TVC will be a vertically positioned stainless steel cylinder with a diameter of 2.75 meters and a height of 2.5 meters. The chamber and thermal shrouds are designed with a diagonal entry, resulting in a wedge-shaped bottom half and top half. This reduces the total height required for opening and operating the chamber as well as facilitating easy loading of the space instrument.

The thermal shroud of the TVC will be able to create an environment between 193K and 353K Two thermal plates will be present to cool areas of the instrument down to 100K if required. The vacuum system consists of two turbomolecular pumps and two cryopumps to reach the ultimate pressure of at least 10e-7 mbar. The vacuum conditions and composition of residual gasses in the TVC will be monitored with an RGA (Residual Gas Analyser) and a QCM (Quarts Crystal Microbalance).

During the calibration of a Space instrument, its orientation relative to the calibration light sources (Optical Ground Support Equipment or OGSE) has to be changed with extremely high accuracy and reproducibility. To achieve this, TNO has selected a vacuum compatible hexapod on a rotation table that meets the stringent accuracy and stability requirements of such an operation. In order to achieve these extreme stability requirements - both in the order of 0.001 degrees - TNO has designed an active thermal system around the hexapod to locally create a thermally stable environment.

During this talk I will discuss the performance of TVC and the instrument manipulation system

9:40am **VT-TuM-6 The Challenges of Heating a Sample in Vacuum***, H. Bekman, **Johannes Velthuis**, F. Molkenboer,* TNO Science and Industry, the Netherlands

Heating a sample up to 400°C in a vacuum system seems not to be complicated, however when this same sample must travel through several vacuum chambers / load locks before arriving at its test location it becomes a greater challenge.

To overcome this stated challenge that is present at EBL2, a large Extreme Ultra-Violet Lithography (EUVL) test facility at TNO that used for EUVL lifetime experiments, we are in the process of designing a special sample holder that can reach, and control the sample temperature between ambient and 400°C.

The sample holder is being developed as part of the EU program, ID2PPAC. The objective of the project is to investigate EUV-material interaction effects at elevated temperatures. This research will contribute applicable knowledge that will result to better material selection in EUVL applications.

It is expected that the last version of the sample holder will require some logic control elements in the sample holder, this because of the limited pinout (number of electrical connections) of the sample holder. The development and testing sub-assemblies of this last version will be time consuming task because a lot of boundary conditions need to be tested.

To ensure that testing of materials can be tested at an earlier phase than before the completion of the last version of the sample holder, two forerunners will be first designed and manufactured.

A complication originates from the EUV power hitting the sample. This EUV power is a heat source that heats up the sample under test. One version will use a low power heater element to control the temperature, this one however is limited in the amount of EUV power the sample can receive, this to prevent overheating the sample.

The second sample holder will be used when the EUV radiation is higher. The sample holder will control the sample temperature by adjusting the backfill pressure between the sample and a colder temperature-controlled element.

By controlling the backfill pressure, the thermal conductance between the sample and the colder temperature-controlled element will change, this method will enable us to cool, and control the temperature of the sample.

During this presentation we will discuss the need for this sample holder, the design, and results of the two first versions of the sample holder. We expect also to be able to present the final design of the last version of the sample holder.

11:00am **VT-TuM-10 Design of ITER Roughing Pump System**, ***Charles Smith**, S. Smith,* US ITER **INVITED**

US ITER is charged with supplying mechanical and cryogenic vacuum roughing components to the ITER Organization as part of the United States' commitment to the ITER Project. The Rough Pump system (RPS) as it is known, connects to the Cryostat vacuum vessel (vacuum volume 8500m^3), Torus vacuum vessel (vacuum volume 1400m^3), Neutral beam injector ports, Type 2 Diagnostic instrumentation, and the Service Vacuum System. The RPS provides support for the roughing of these volumes, backing to localized high vacuum pumping stations, and regeneration of the Torus and Cryostat cryopumps. Due to the nature of the ITER machine, traditional gasses (nitrogen, air, helium, etc.) are pumped along with hydrogen isotopes (H_2, D_2, T_2, and combinations thereof). Therefore, the RPS system has specialized roughing trains dedicated to handling each application.

The Non-Active Roughing Systems, defined as systems in which tritium is not expected to be present, employ traditional commercially available pumping technologies. The Non-Active pumping system supports the Cryostat volume roughing, Cryostat Cryopump regeneration, and the Non-Active portion of the service vacuum system. The Active Roughing Systems, defined as systems in which at least some level of tritium is expected to be present, employ all-metal seal roughing pumps coupled with cryogenic systems in the process flow. These all-metal seal pumps are being specifically designed for this application. The cryogenic systems are located in the process stream between the ITER machine vacuum volumes and the active mechanical roughing pumps in order to capture both the hydrogen isotopes and water vapor prior to entering the mechanical pump skids. The cryogenic systems consist of Cryogenic Viscous-Flow Compressors (CVCs) and Condensable Vapor Devices (CVDs). Supercritical and gaseous Helium are supplied from the centralized cryogenic plant and distributed to the RPS systems via Cryogenic Transfer Lines (CTLs) connected to three Cryogenic Distribution Boxes (CDBs) which distribute the cryogens to the CVCs and CVDs using cryogenic jumper connections.

This talk will discuss the unique aspects of the design and requirements of the RPS mechanical and cryogenic pumping elements which allow ITER to engage in the critical science of developing sustainable burning plasma operations to facilitate the design and construction of commercial fusion power plants.

11:40am **VT-TuM-12 Monte Carlo Simulation Studies to Support an Integrated Design for the Cryogenic Vacuum Systems of the Einstein Telescope**, ***Xueli Luo**,* Karlsruhe Institute of Technology, Institute for Technical Physics, Germany*; S. Hanke, K. Battes, C. Day,* Karlsruhe Institute of Technology (KIT), Germany

Europe is going to develop a third-generation underground gravitational wave (GW) observatory, known as the Einstein Telescope (ET). It is designed as a novel equilateral triangle with 10 km long arms and the detectors in each corner. Any two adjacent arms compose two independent interferometers. One interferometer will detect low-frequency gravitational wave signals (LF), while the other will be optimized for operation at higher frequencies.

In order to reduce seismic noise, thermal noise and other systematic noise, the whole system will be 200 to 300 m underneath the ground; the beamline pipes, the suspension towers and the cryostat containing the mirror require ultra-high or high vacuum conditions; and the main optics will partly be cooled to cryogenic temperatures below 20 K. In this way, the GW detecting sensitivity of ET will be significantly increased compared to the current advanced detectors (Virgo, LIGO) and the frequency band will be expanded to lower frequencies. The integral ET vacuum system comprises three different parts: (i) the beamline vacuum characterised by outgassing from the pipe walls, (ii) the tower vacuum characterised by outgassing from the suspension arrangement, and (iii) the cryogenic vacuum systems around the LF mirror.

In this paper, a Test Particle Monte Carlo model has been established with the KIT in-house code ProVac3D, to allow for a system analysis of the cryogenic vacuum area. It assesses the impinging rate of residual gas on the cryogenic mirror, depending on the particle sources from the beamline pipes and from the tower, which are systematically varied. With that, the expected speed of frost formation is estimated, which is critical due to degradations of the optical performance, and helpful information on engineering limits are derived. These simulation results are useful to find how far the cryopump section will influence the condition in the warm beamline pipe and the gas flow rate to the optical mirror. As a second major contribution, a shielding concept around the mirror is presented which reduces the gas load to a level fulfilling the requirements.

Tuesday Morning Break, November 8, 2022

Exhibitor Technology Spotlight Workshops
Room Hall A - Session EW-TuMB

Exhibitor Technology Spotlight Session I

Moderator: Christopher Moffitt, Kratos Analytical Inc

10:20am **EW-TuMB-2 Edwards Vacuum Presentation - The Future of Vacuum I & II: A Review of Safety Considerations in the Design and Operation of Vacuum Systems*, Andrew Chew,*** Edwards

The Vacuum Industry is, characteristically, comprised of an extremely wide spectrum of applications, techniques and equipment requirements. The assurance of safe operating conditions is a common and unifying factor. This presentation will describe some challenges and requirements for the safe operation of vacuum systems with respect to pumps, gauges and exhaust gas abatement.

Exhibitor Technology Spotlight Workshops
Room Hall A - Session EW-TuL

Exhibitor Technology Spotlight Session II

Moderator: Christopher Moffitt, Kratos Analytical Inc

12:40pm **EW-TuL-3 New Developments in Surface Analysis from Thermo Fisher Scientific*, Adam Bushell,*** *T. Nunney, P. Mack, R. Simpson,* Thermo Fisher Scientific, UK

In this presentation we will detail the latest developments in the Surface Analysis portfolio from Thermo Fisher Scientific

1:00pm **EW-TuL-4 PHI Surface Analysis Solutions: No Compromise*, Jennifer Mann,*** Physical Electronics

Physical Electronics (PHI) is the only manufacturer offering surface analysis products for all three main analytical techniques – X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES) and time-of-flight secondary ion mass spectrometry (TOF-SIMS). This presentation will discuss recent developments in all three product lines. Our fully automated XPS system offers unprecedented value not found in conventional XPS instruments, by using multiple techniques covering a full range of energy - from conduction band with low energy inverse photoemission spectroscopy (LEIPS) to core-level excitation with hard X-ray photoelectron spectroscopy (HAXPES). A TOF-SIMS instrument from PHI is optimized for the highest sensitivity elemental and molecular analysis. Our scanning AES instrument is optimized for high magnification chemical imaging and has increased versatility with multiple optional technique add-ons and accessories for specialized experiments.

1:20pm **EW-TuL-5 EnviroMetros – A Novel Surface and Multilayer Thin Film Analysis Tool*, Andreas Thissen,*** SPECS Surface Nano Analysis GmbH, Germany

Ultrathin films and 2D materials are continuously gaining relevance for modern devices. Thus, there is growing interest in chemical analysis of such multilayer systems and their surfaces. A detailed characterization of stoichiometries, composition and depth distribution of elements is needed. The novel EnviroMetros series provides the perfect routine analysis tools for this field of research and development by combining large sample and wafer handling with a variable information depth photoelectron spectrometer. In combination with optical and other analytical techniques it allow for a depth dependent composition analysis of unsurpassed precision, reliability and repeatability.

1:40pm **EW-TuL-6 AFM - The Instrument of Choice for Twisted Graphene Preparation and Characterization*, Ted Limpoco,*** Oxford Instruments Asylum Research Inc.

2D materials are currently a hot topic in the materials research community as they have been shown to exhibit novel mechanical, optical and electrical properties. Graphene, specifically twisted graphene, exhibits Moiré superlattices that are of particular interest. These samples are prepared by imaging the graphene flakes, cutting them, rotating, and transferring them to new substrates in a specific order. Precise control over the manipulation of graphene and in-depth characterization of the resulting sample properties are crucial steps in the preparation of new and performant 2D material-based devices. To achieve this, a high-performance Atomic Force Microscope (AFM) is the instrument of choice. We present here the best imaging modes and setups to facilitate the twisted graphene sample preparation and characterization. Topography, conductivity, friction and piezoelectric data will be shown and discussed in the context of sample preparation and the expected sample properties.

2:00pm **EW-TuL-7 Automated, High-Performance X-Ray Photoelectron Spectroscopy System for Advanced Analysis of Solid-State Energy Materials and Systems*, Chris Blomfield,*** Kratos Analytical Inc., UK

Sensitivity to low material concentrations and the ability to resolve different chemical states are fundamental aspects of surface analysis with XPS, which determine the interpretation and the understanding of the revealed chemistry. Modern automation allows more samples to be analyzed with the full capabilities of the highest-performing XPS instrument, the Kratos Axis Supra$^+$, without intervention. Once samples are physically loaded, analyses are submitted through the computer interface, utilizing multiple cameras for location identification, which can be done remotely.

Current research into energy storage materials has driven the development of sample holders to accommodate electrical contacts for operando measurement while biasing or flowing current, along with sample heating capability for accelerated aging studies. The multi-contact stage in the Axis Supra$^+$ spectrometer accommodates these specialized holders, supplying 4 electrical contacts to be used for these analyses, while still accepting all the standard sample platens for high throughput analysis. An inert sample transfer version of these multi-contact holders has also been developed, which allows the sample to be loaded and electrical connections made in a glove box and then loaded into the spectrometer without exposure to atmosphere.

Cluster ion sources for sputter depth profiling have greatly expanded soft materials analysis, opening up previously inaccessible interfaces to the power of XPS analysis. Coupling the multi-contact capability with an advanced, dual mode argon gas cluster ion source (GCIS) allows for profiling of all materials in the sample system, including organic compounds not previously possible. The cluster mode is able to profile light ion materials without the artifacts inherent in monoatomic sputter-etching of these materials. Additional analytical techniques, such as Ag-Lα HAXPES, ISS, UPS, AES, REELS and IPES are all possible on the Supra$^+$ and additional sample preparation chambers can be added, such as a station for deposition or the high-pressure, high-temperature gas reaction cell for catalysis experiments and measurement.

2D Materials Technical Group
Room 303 - Session 2D+MI-TuA

2D Materials: Heterostructures, Twistronics, and Proximity Effects

Moderators: Francesca Tavazza, National Institute of Standard and Technology, **Suyang Xu**, Harvard University

2:20pm **2D+MI-TuA-1 Strategies for Controlling Structure and Magnetic Texture in 2D Magnets*, Frances Ross,*** MIT*; J. Klein,* MIT, USA **INVITED**

Electronic devices that incorporate two dimensional (2D) materials often require contacting or patterning the 2D layer for their fabrication. This is particularly important when we aim to build exciting new nanoscale magneto-electric devices based on 2D magnetic materials. CrSBr is such a 2D magnet that shows stability in air, giving this material a key advantage in practical device fabrication compared to other, less stable 2D magnets. Here we discuss strategies for controlling the structure and properties of CrSBr and related 2D magnets at the local, nanoscale level. We approach this via transmission electron microscopy, based on promising results for other 2D materials. We first discuss local control of structure. We find that electron beam irradiation in a scanning transmission electron microscope (STEM) induces a surprising structural change, where Cr atoms migrate into the van der Waals gap to create a new phase with layer direction (and, in theory, magnetization) perpendicular to the initial layers. The ability to modulate the magnetization direction deterministically is of great interest for quantum devices. Furthermore, since we find that defects in this material can be optically active and correlated with magnetic order and phases, the ability to use STEM to control individual defects will ultimately help to achieve precise control of the material's properties. We next discuss strategies for contacts. For other 2D materials, the 2D/3D contact resistance is known to improve when the contact layers have fewer grain boundaries. We therefore focus on epitaxial growth of metals and other 3D crystals onto the 2D surface. We show how *in situ* TEM imaging helps to clarify the growth mechanisms and interface structures formed during single crystal or heterostructured metal growth on graphene, hBN and transition metal dichalcogenides. We then explore how nucleation and epitaxy phenomena play out for pristine and patterned CrSBr and other 2D magnets. Overall, we conclude that atomic level structural and chemical modification are crucial for understanding properties and designing devices that use the exciting properties of the new 2D magnets. We suggest that rapidly advancing *in situ* TEM instrumentation promises exciting future opportunities where nanoscale growth and patterning create complex devices based on 2D materials.

3:00pm **2D+MI-TuA-3 Bidirectional Phonon Emission in van der Waals Heterojunctions During Ultrafast Charge Transfer*, Aditya Sood,*** Stanford University

Photoinduced charge transfer in van der Waals heterostructures occurs on ultrafast timescales of order 100 fs, despite the weak interlayer coupling and momentum mismatch. Little is understood about the microscopic mechanism behind this fast process and the role of the lattice in mediating it. Here, using femtosecond electron diffraction, we directly visualize lattice dynamics in photoexcited heterostructures of WSe_2/WS_2 monolayers. Following selective excitation of WSe_2, we measure unexpectedly concurrent heating of both WSe_2 and WS_2 on a 1 picosecond timescale, corresponding to an "apparent" interlayer thermal conductance that is >100x larger than that due to phonons alone. Using first-principles calculations, we identify a fast channel, involving an electronic state hybridized across the heterostructure, enabling phonon-assisted interlayer transfer of photoexcited electrons. Phonons are emitted in both layers on femtosecond timescales via this channel, consistent with the simultaneous lattice heating observed experimentally. Taken together, our work indicates strong electron-phonon coupling via layer-hybridized electronic states – a novel route to control energy transport across atomic junctions.

4:20pm **2D+MI-TuA-7 Understanding Structural, Chemical, and Number of Layer-Dependent Properties in 2D Lateral and Vertical Structures for Subsequent Optical Measurements***, U. Kaiser,* ***Michael Mohn,*** University of Ulm, Germany **INVITED**

Properties of 2D materials can manifest at very different length scales. Charge density waves, magnetic ordering, inter- and intralayer excitons are studied also to understand their atomistic origin. Moreover, starting from exciting properties of low-twist angle graphene, twisted transition metal dichalcogenides are now explored, whereby the future of moiré superlattices is also dependent on reliable twist angle control. In addition, interfaces of transition metal dichalcogenide heterostructures such as Janus monolayers or lateral heterostructures have potential applications in optoelectronics, however very critical for carrier and exciton transport is that they are atomically sharp.

Here we use the low-voltage- spherical and chromatic aberration-corrected transmission electron microscope to measure and introduce structural and chemical variations in free-standing 2D materials on the atomic scale. In-situ and ex-situ optical measurements are performed and together with quantum-mechanical calculations their atomic-structure-based properties are understood.

We first report on advances in TEM sample preparation both for oxygen-sensitive TMDs as well as describe our sample platform to relate atomic defects in 2D materials produced by TEM with subsequent measurements in stacked devices. Then we describe studies on electron-beam-induced defects and observe the migration paths and associated property changes in a variety of single and few-layered free-standing structures of transition metal di-chalcogenides (TMDs) and transition metal phosphorus tri-chalcogenides (TMPTs). We also investigate the twist-angle-dependent moiré pattern formation in bilayers of TMDs by theoretical prediction-followed TEM experiments. From the comparison of monolayer, bi-layer and 2° twisted bilayer experimental images, we determine twist-angle-induced inhomogeneous stacking-related localized strain in the layers as well as the twist-angle-induced changes of the interlayer excitons located in the low-loss range of the EELS spectrum. We further report on the number of layer-dependent electronic properties of Pt-dichalcogenide family. We also show proof-of-principle experiments in which we transfer electron-exposed TMD flakes from a TEM grid to arbitrary substrates and measure the produced defects in photoluminescence and transport measurements. Moreover, the investigated lateral heterostructures show near-atomically sharp junctions with a typical extent of 3 nm for the covalently bonded $MoSe_2$-WSe_2 interface, determined by high-resolution transmission electron microscopy. This explains the considerably narrowed optical transition linewidth in the photoluminescence, reflectance contrast and Raman spectroscopy.

5:00pm **2D+MI-TuA-9 Determination of Band Offsets in Semiconductor Heterostructures (2D/3D) by Using XPS*, Mohamed Nejib Hedhili,*** *⍰. NG, B. Ooi,* King Abdullah University of Science and Technology, Saudi Arabia

Electrical and optical properties of heterojunction semiconductors are heavily influenced by the relative alignment of their energy band edges at the interface [1]. That is why the knowledge of this alignment is crucial for the design of heterostructure devices. In this regard, high-resolution X-ray photoemission spectroscopy (HR-XPS) has been shown to measure the valence band offset of heterojunction semiconductors quite accurately [2]. In this report, we present a study devoted to the characterization of 2D/ 3D heterojunction semiconductor materials using a myriad of techniques including HR-XPS, scanning transmission electron microscopy (STEM), atomic force microscopy (AFM), micro-Raman, absorbance, and microphotoluminescence spectroscopy.

The samples for this study were prepared by depositing an epitaxial GaN ($In_{0.15}Al_{0.85}N$) thin layer with molecular beam epitaxy (MBE) on chemically vapor deposition (CVD) grown single-layer (SL) MoS_2/c-sapphire (WSe_2/c-sapphire) substrates. The formation of SL of MoS_2 (WSe_2)was crucial to device properties and hence was confirmed by using both STEM and AFM techniques. HR-XPS analysis of samples was performed in two-steps to measure the valence band discontinuity for GaN ($In_{0.15}Al_{0.85}N$) / SL of MoS_2 (WSe_2) heterojunction interface. In first step, the core level binding energies with respect to the valence band maximum in both GaN ($In_{0.15}Al_{0.85}N$) and MoS_2 (WSe_2) bulk films were measured. Second, the subsequent measurements on the separation between Ga (In) and Mo (W) core levels for GaN ($In_{0.15}Al_{0.85}N$) thin layer grown SL-MoS_2 (SL-WSe_2)was measured. The valence band and conduction band offset values are determined.

The band alignment parameters determined here provide a route toward the integration of group III nitride semiconducting materials with transition metal dichalcogenides (TMDs) for designing and modeling their heterojunction-based electronic and optoelectronic devices.

References:

[1] U. Gnutzmann and K. Clausecker, Appl. Phys. 3, 9 (1974).

[2] J. C. Bernède, L. Cattin, P. Predeep, XPS Study of the Band Alignment at the Interface

ITO/CuI, Technology Letters 1 (1), 2 (2014).

5:20pm **2D+MI-TuA-10 Investigation of a Novel Layer-by-Layer Growth Methodology for Surface Metal-Organic Frameworks***, **Nicholas Stucchi,*** Clarkson University

The fabrication of highly ordered and crystalline surface-confined metal-organic frameworks (SURMOFs) has garnered interest in applications such as catalysis, gas storage, and gas separation. At present, the state of the art of SURMOF fabrication is a layer-by-layer (LBL) growth, wherein a functionalized substrate undergoes sequential immersions in solutions of the desired metal or ligand. This LBL strategy is commonly performed using gold substrates modified with carboxylate-terminated self-assembled monolayers (SAMs) which act as an initial nucleation site for the metal cluster. Careful control over deposition conditions and reaction times results in the formation of crystalline SURMOFs with tunable thicknesses. However, this technique is limited to substrates that can undergo the necessary SAM functionalization as well as being highly sensitive to the deposition conditions. I will discuss the development of a new LBL methodology that utilizes a pre-formed covalent-organic framework (COF) on the surface of highly oriented pyrolytic graphite (HOPG) as the template for SURMOF growth. The COF template should have the same geometry and a lattice parameter close to that of the desired SURMOF to minimize the strain of the first few layers. As such, COF-366-Zn was chosen as the template for UiO-67, which has a 3% lattice mismatch between the COF template and MOF. The COF was reacted with isonicotinic acid (INA) in which the pyridine axially coordinates to the zinc centers of the COF and the exposed carboxylate moieties of the INA serve as nucleation sites for the zirconium acetate clusters of UiO-67. The SURMOF was formed following several sequential reactions in the cluster and benezene-1,4-dicarboxylic acid (BDA) ligand solutions. The COF and initial INA binding will be characterized by scanning tunneling microscopy (STM) and Fourier-Transform Infrared (FTIR) spectroscopy. Atomic force microscopy (AFM) will be used to characterize the LBL growth of UiO-67. The crystallinity of the SURMOF will be determined using diffraction techniques.

Atomic Scale Processing Focus Topic
Room 317 - Session AP+PS+TF-TuA

Thermal Atomic Layer Etching

Moderators: Silvia Armini, IMEC, Belgium, **Eric A. Joseph**, IBM Research Division, T.J. Watson Research Center

2:20pm **AP+PS+TF-TuA-1 Thermal Atomic Layer Etching: The Right Etch Technology at the Right Time***, **Andreas Fischer**, A. Routzahn, R. Gasvoda, J. Sims, T. Lill,* Lam Research Corporation **INVITED**

Thermal atomic layer etching is rapidly becoming an important complementary processing technology in manufacturing of advanced logic and memory semiconductor devices.Critically, stacked chip architectures such as 3D NAND, 3D DRAM or Gate-all-around devices require conformal isotropic etching to remove material such as HfO_2 or SiGe in hard-to-reach locations with aspect ratios that can be greater than 50:1.To achieve repeatable device performance throughout a 3D stack, the removal rate (etch per cycle) of the etched material during an etch process need to be controlled such that the overall etch is the same from top to bottom of the device stack.In this work we studied HfO_2-based 3D NAND test structures with an aspect ratio of more than 50:1. Etching was performed via ligand exchange with dimethyl-aluminum chloride (DMAC) after surfaces had been fluorinated with hydrogen fluoride (HF).Fluorination studies on blanket films revealed that fluorination efficiency is improving for pressures in the Torr range compared to previous millitorr experiments and that only temperatures above 250°C increased the fluorine concentration in HfO_2 significantly whereas fluorine levels were unchanged between 150°C and 250°C.Regarding etch rates in these 3D NAND structures, we found that the horizontal etch rate of HfO_2 as a function of depth (depth loading) depended on the DMAC dosing but was nearly independent on the HF dose.The HF dose and the process pressure were key to increasing the overall etch amount per cycle (EPC).With the highest tested HF dose of 192 Torr*s and a total process pressure of 8 Torr, we achieved a uniform etch amount of 0.6 nm per cycle.In addition, we investigated the impact of film quality and film coating conformality in these structures on the depth loading in the succeeding ALE processes.Type of precursor, precursor dosing, deposition rate as well as substrate temperature played a fundamental role in controlling the film quality and conformality of the deposited HfO_2 layers inside high aspect ratio holes.

3:00pm **AP+PS+TF-TuA-3 Atomic Layer Etching of Titanium Nitride with Surface Modification by Cl Radicals and Rapid Thermal Annealing***, N. Miyoshi,* Hitachi High Technologies America Inc., Japan*; **Nicholas McDowell,*** Hitachi High Technologies America Inc.*; H. Kobayashi,* Hitachi Global Storage Technologies Inc, Japan

Thermal atomic layer etching (ALE) is a promising method for isotropic etching with atomic level precision and high conformality over three-dimensional structures. Due to these characteristics, thermal ALE will be a crucial component of etching the next generation of semiconductor devices. In this study, a thermal ALE process for titanium nitride (TiN) films was developed using surface modification with a Cl2/Ar downstream plasma followed by infrared (IR) annealing of the films. The oxygen-free Cl2-based plasma was adopted to allow a highly selective etch with respect to various materials. Evaluations showed spontaneous etching of TiN during radical exposure can be suppressed at a surface temperature of −10 ºC. Evaluations demonstrated that this process is self-limiting with respect to both radical exposure and IR annealing. With repeated steps of self-limiting radical exposure and IR annealing, TiN was etched at 2.0 nm/cycle, while no thickness change was observed for poly-Si, SiO2, Si3N4, W, and HfO2. The selectivity of amorphous carbon was shown to be higher than 4. X-ray photoelectron spectroscopy analysis showed that the N in the TiN surface layer is spontaneously removed by Cl radical exposure as NClx and NOxCly (Due to residual O in the chamber) species and the film is left with a modified surface layer of TiClx. The remaining TiClx modified layer can then be desorbed by IR annealing, returning the surface layer to its original condition (pristine TiN).

3:20pm **AP+PS+TF-TuA-4 Thermal Atomic Layer Etching (ALE) of Metal Oxides by Chlorination and Ligand Addition using SO_2Cl_2 and Tetramethylethylenediamine (TMEDA)***, **Jonathan Partridge**, J. Murdzek, S. George,* University of Colorado Boulder

The thermal ALE of many metal oxides, such as Al_2O_3, HfO_2 and ZrO_2, can be accomplished using the fluorination and ligand-exchange mechanism.For other metal oxides, this reaction pathway is not viable because of difficulty finding appropriate ligand-exchange precursors.Fortunately, other etching mechanisms are possible based on ligand addition instead of ligand exchange.During ligand addition, the modified surface layer is volatilized by adding a ligand to the surface metal complex.This study will illustrate the ability of chlorination and ligand addition to etch a variety of first-row transition metal oxides.

Thermal ALE of Fe_2O_3, CoO, NiO and ZnO was demonstrated with sequential exposures of SO_2Cl_2 for chlorination and tetramethylethylenediamine (TMEDA) for ligand addition at 250°C.Using CoO as an example, SO_2Cl_2 chlorinates CoO to form $CoCl_2$ on the CoO surface.TMEDA then undergoes ligand addition with $CoCl_2$ surface species to form a volatile $CoCl_2$(TMEDA) etch product. X-ray reflectivity experiments measured CoO etch rates of 2-3 Å/cycle at 175 - 250°C.The volatile etch products were also identified using a new reactor equipped with a quadrupole mass spectrometer (QMS).The $CoCl_2$(TMEDA) etch product was observed by QMS analysis during TMEDA exposures.CoO etching also involves oxygen loss.Thermochemical calculations indicate that the oxygen could be lost by the formation of SO_3 or O_2.These oxygen products have not been confirmed by QMS analysis.SO_3 is unstable and difficult to observe by QMS.The cracking pattern of SO_2Cl_2 interferes with O_2 detection.

For the other metal oxides, QMS analysis observed $FeCl_2(TMEDA)^+$ ion signals for Fe_2O_3 etching during the TMEDA exposures. $NiCl_2(TMEDA)^+$ ion signals were also monitored for NiO etching during the TMEDA exposures. In addition, $ZnCl(TMEDA)^+$ ion signals were measured for ZnO etching during the TMEDA exposures.Chlorination and ligand-addition was also explored for the thermal ALE of V_2O_5, CuO, Cr_2O_3 and MnO_2. Unfortunately, V_2O_5 and CuO spontaneously etched during the SO_2Cl_2 exposure to form $VOCl_3$ and $CuCl_3$, respectively. Etch products containing TMEDA were not observed for Cr_2O_3 and MnO_2. This work illustrates that sequential exposures of SO_2Cl_2 and TMEDA will be useful for the thermal ALE of a variety of metal oxides that have stable metal chlorides and can not be etched using the fluorination and ligand-exchange mechanism.

4:20pm **AP+PS+TF-TuA-7 Thermal Atomic Layer Etch Processes in Semiconductor Manufacturing Challenges and Opportunities***, **Gert Leusink,*** TEL Technology Center, America, LLC **INVITED**

Driven by ever-increasing complexity in materials and structures, process technology requirements in semiconductor device manufacturing have evolved to control at the atomic level. In recent years, atomic level processing has been introduced in deposition, etching, and (wet) cleaning.

Chemically selective and/or area-selective processes can be an efficient way to meet future manufacturing requirements[1,2]. Furthermore, damage free low temperature thermal processes will be needed to enable precise control in 3D structures with small CDs and high aspect ratios[3].

In this talk, we will review some of the fundamentals and challenges in thermal Atomic Layer Process technologies for advanced semiconductor device manufacturing. We will discuss recent trends in thermal Atomic Layer Etching (ALE) and show examples how these processes may be used to address some of the critical challenges in cleaning, etching and patterning applications in the manufacturing of 3D devices.

33. *Perspective: New process technologies required for future devices and scaling*, R. Clark [https://aip.scitation.org/author/Clark%2C+R]*et al*, APL Materials 6, (2018)
34. *Overview of atomic layer etching in the semiconductor industry,* Kanarik, K*et al,* Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films, 33(2), 020802
35. 3-D Self-aligned Stacked NMOS-on-PMOS Nanoribbon Transistors for Continued Moore's Law Scaling, C. -Y. Huang et al, IEDM 2020

5:00pm **AP+PS+TF-TuA-9 Thermal Atomic Layer Etching (ALE) of InGaP:Processing Chemistry and Removal of Surface Defects***, **Ross Edel**, T. Nam, S. George,* University of Colorado Boulder

Thermal ALE of crystalline indium gallium phosphide (InGaP) has been developed to extend thermal ALE to phosphide semiconductor materials. These phosphide semiconductor materials are widely used as red light-emitting diode (LED) devices. Native oxides and surface defects on LED devices can lead to electron/hole pair recombination that reduces their light output. In particular, the light output can be significantly reduced on smaller devices having high surface-to-volume ratios. The surface defects are believed to be formed by energetic ion species from previous plasma processing steps. Thermal ALE may provide a method to remove the native oxides and surface defects without causing additional damage.

This work was conducted using a new apparatus that combines a hot wall ALD/ALE reactor with *in vacuo* Auger spectroscopy. This apparatus allows the InGaP sample to be characterized throughout the thermal ALE process without exposure to atmosphere. The thermal InGaP ALE was performed using static, sequential hydrogen fluoride (HF) and dimethylaluminum chloride (DMAC) exposures. The HF/DMAC exposures were able to achieve InGaP etch rates of 0.5–1.0 Å/cycle at temperatures from 300–330 °C, respectively. The etch rates were measured for thin InGaP films on GaAs substrates using *ex situ* spectroscopic ellipsometry.

Etching with only HF/DMAC exposures could produce a chemically distinct top layer. This top layer was believed to be caused by the conversion of the InGaP native oxide to Al_2O_3 or $AlPO_4$ by DMAC. However, this conversion could be avoided by first removing the InGaP native oxide using sequential HF and trimethylaluminum (TMA) exposures. The HF/TMA exposures were able to achieve native oxide etch rates of >1 Å/cycle at temperatures above 300 °C. The underlying InGaP could then be reliably etched with no top layer formation. In the optimized process, the InGaP native oxide was first removed using sequential HF and TMA exposures. Subsequently, the InGaP was etched using sequential HF and DMAC exposures.

The removal of surface defects by ALE was also studied using *ex situ* X-ray photoelectron spectroscopy (XPS). InGaP samples damaged by Ar^+ ion sputtering were analyzed before and after thermal ALE. The XPS analysis focused on the phosphorus XPS signals that revealed the sputter damage. The proportion of the phosphorus XPS signal intensity attributed to sputter damage was found to decrease versus number of thermal ALE cycles.

5:20pm **AP+PS+TF-TuA-10 Thermal Atomic Layer Etching of MoS2 Films***, **Jake Soares**,* Boise State University*; A. Mane,* Argonne National Laboratory*; S. Hues,* Boise State University*; J. Elam,* Argonne National Laboratory*; E. Graugnard,* Boise State University

2D materials can offer promise for a wide range of application within semiconductor manufacturing. Of these materials, molybdenum disulfide (MoS_2) is of great interest due to its high mobility, measured on/off ratio, tunable band gap, and a film thickness ideal for scaling. In order to move this material closer to integration with semiconductor manufacturing, a great amount of processing control is required. Atomic layer processing techniques can accommodate this needed precision, where both the deposition and removal of MoS_2 has been studied. In this work we report a thermal atomic layer etching (ALE) process for MoS_2 using MoF_6 and H_2O as precursor reactants. Here, we will discuss atomic layer etching of both amorphous as-deposited and crystalline MoS_2 films. In–situ quartz crystal microbalance measurements (QCM) indicate removal of as-deposited films when switching from a deposition chemistry (MoF_6 + H_2S) to the proposed etching chemistry (MoF_6 + H_2O). Saturation curves for the etching process were additionally identified with QCM by studying the mass gained per cycle versus the precursor dose duration. Films deposited on planar coupons were characterized with ellipsometry and X-ray reflectance to determine the etch per cycle. We propose the chemical reaction equations for the etch process as guided by residual gas analysis of byproduct formation, Gibbs free energy calculations, and QCM mass ratio analysis. After ALD and subsequent ALE processing, we produced few layer crystalline MoS_2 films once annealed. With the many application of both amorphous and crystalline MoS_2, this work helps to identify and expand current atomic layer processing chemistries.

5:40pm **AP+PS+TF-TuA-11 Atomically-Precise Surface Processes: From Molecular Mechanisms to Realistic Devices***, **Andrew Teplyakov**,* University of Delaware

The atomic-level precision in designing surfaces and nanostructures is quickly making its way from the one-off laboratory investigations into chemical manufacturing. However, in order to make the applications feasible, fundamental understanding of the mechanisms of surface reactions leading to the formation of the desired surface structures is needed. A great deal of progress has been made over the years in uncovering reactions behind atomic layer deposition (ALD), but much more limited information is available about atomic layer etching (ALE), although both processes are often required to build the components of present and future microelectronics.

This talk will highlight recent work on understanding the reactions for metal and metal oxide deposition on functionalized (and patterned) surfaces and on recent advances in ALE of complex materials, specifically focused on tertiary alloys, such as CoFeB, used in magnetic tunnel junctions. I will outline the work needed to understand the mechanisms of these processes that can be further used to improve the control over atomically-precise manufacturing methods and to reduce the use of hazardous procedures. The relatively well-understood ALE procedures that include oxidation or chlorination as the first half-cycle of ALE of such materials and introduction of a bidentate ligands (such as acetylacetonates) to remove complex materials uniformly and with atomic-level control will be extended to describe the potential use of much milder conditions and reagents. A combination of experimental and computational methods will be used to make this analysis possible.

6:00pm **AP+PS+TF-TuA-12 Deposit and Etchback Approach for Ultrathin and Continuous Films Using Atomic Layer Deposition and Atomic Layer Etching***, J. Gertsch, E. Sortino, V. Bright, **Steven George**,* University of Colorado Boulder

Ultrathin and continuous films are desirable in many devices such as MIM capacitors and ferroelectric tunnel junctions. Atomic layer deposition (ALD) methods are often used to deposit these ultrathin films. However, nucleation delays can lead to pinholes and thickness variations in ALD films. Higher quality ultrathin and continuous films can be obtained using a deposit and etchback approach using ALD and atomic layer etching (ALE). In this method, an ALD film is deposited to a thickness greater than the desired thickness to reduce the number of pinholes and form a more continuous ALD film. Subsequently, the ALD film is etched back to a smaller thickness using ALE.

The deposit and etchback approach can be illustrated for Al_2O_3 ALD in metal-insulator-metal (MIM) capacitors [1]. The benefit of the deposit and etchback approach can be measured by the percentage yield of MIM capacitors based on an $Ag/Al_2O_3/Al$ structure that do not have an electrical short. Al_2O_3 ALD was performed using sequential exposures of trimethylaluminum (TMA) and H_2O as the reactants. Thermal Al_2O_3 ALE was conducted using sequential exposures of HF and TMA as the reactants. The experiments confirmed that the device yield was improved using the deposition and etchback approach. For example, using device areas of 0.01 mm^2, Al_2O_3 ALD films that were grown to 5 nm in the MIM capacitor displayed a yield of 30-40%. In contrast, Al_2O_3 ALD films that were grown to 24 nm and then etched back to 5 nm to form the MIM capacitor displayed a much higher yield of 65-75%.

Additional experiments revealed that a portion of the yield improvement can be attributed to the fluorination of the Al_2O_3 ALD films [1]. Fluorination produces a volume expansion when forming AlF_3 from Al_2O_3. This volume expansion may produce a compressive stress that helps to close the pinholes. The deposit and etchback approach can also be used to improve the performance of $Hf_{0.5}Zr_{0.5}O_2$ (HZO) ferroelectric tunnel junctions. Thicker HZO films are needed to crystallize HZO films by thermal annealing. However, thinner HZO films are required for the best devices. Recent experiments have shown that the deposit and etchback approach can substantially improve the device performance of HZO ferroelectric tunnel junctions [2].

[1] J.C. Gertsch et al., "Deposit and Etchback Approach for Ultrathin Al_2O_3 Films with Low Pinhole Density Using Atomic Layer Deposition and Atomic Layer Etching", *J. Vac. Sci. Technol. A***39**, 062602 (2021).

[2] M. Hoffmann et al., "Atomic Layer Etching of Ferroelectric Hafnium Zirconium Oxide Thin Films Enables Giant Tunneling Electroresistance", *Appl. Phys. Lett.* **120**, 122901 (2022).

Applied Surface Science Division
Room 320 - Session AS+EM+SE-TuA

Surface Analysis Using Complementary Techniques

Moderators: Samantha Rosenberg, Sandia National Laboratory, **Carl A. Ventrice, Jr.**, SUNY Polytechnic Institute

2:20pm **AS+EM+SE-TuA-1 Origins of the Emergent Phenomena at Oxide Interfaces Studied with Complementary X-Ray Spectroscopic and Scattering Techniques***, **Alexander Gray,*** Temple University **INVITED**

Atomic-level design of complex-oxide heterostructures that exhibit functional electronic and magnetic phenomena has become a diverse and vibrant subfield of condensed matter physics and material science. Of particular interest are the material systems wherein rich physics and intricate interplay between various degrees of freedom at the interface give rise to functional properties not observed in the constituent materials. Detection and characterization of these interfacial properties present a unique practical challenge due to the lack of direct yet non-destructive techniques that are capable of probing minute changes in the electronic and magnetic states at a buried interface with element specificity and Ångstrom-level spatial resolution. In this talk, I will discuss several recent studies in which we utilized a combination of complementary x-ray spectroscopic and scattering techniques to understand the origins of the emergent low-dimensional ferromagnetic states in $LaNiO_3/CaMnO_3$ and $CaRuO_3/CaMnO_3$ superlattices. Depth-resolved standing-wave photoemission spectroscopy was used to probe the depth-dependent changes in the electronic states, while soft x-ray resonant magnetic scattering was used to extract the element-specific magnetic profile of the interface. The results of the experiments were compared to and interpreted using state-of-the-art first-principles theoretical calculations.

This work was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Materials Sciences, and Engineering Division under Award DE-SC0019297.

3:00pm **AS+EM+SE-TuA-3 Multi-Technique Forensic Analysis by Co-Incident XPS & Raman Imaging***, **Robin Simpson**, P. Mack,* Thermo Fisher Scientific, UK

For more than 100 years fingerprint analysis has been ubiquitous in the forensic sciences and is still a core method for identifying individuals in forensics. The techniques used to analyze fingerprints are either structural, for identifying the features of the fingerprints, or chemical, characterizing the composition of the deposited material. Many of these chemical characterization techniques are destructive to the sample preventing any further analysis from being performed or the sample from being preserved as evidence for a later date. Here we show the benefits of using XPS to analyze fingerprints, where the elemental and chemical state composition of a sample can be acquired non-destructively from the top 10 nm of the surface.

In this investigation, we build on our previous work investigating fingerprint analysis. In that study, XPS and XPS mapping techniques were utilized to identify and characterize the contamination of fingerprints. Fingerprints contaminated with TiO-$_2$, and PbO deposited on the silicon wafer can be chemically mapped and visualized using XPS using principal component analysis, PCA.

In this study, we also discuss other examples of forensic analysis including the identification of pharmaceutical substances using complementary XPS and Raman analysis. To achieve this an "over the counter" multi-component analgesic tabletwas crushed to a powder form and deposited onto the substrate. The powder is mapped rapidly using XPS imaging and the data is processed by PCA. This information was used to identify areas for further analysis by high-resolution XPS and Raman. Further Raman analysis was used to characterize the composition of the 3 areas of the sample and identify the compounds contained in them. These are shown to be aspirin, paracetamol, and caffeine through comparison with known sample spectra in the OMINC Raman spectral database.

In the final two examples of forensic analysis workflows in this presentation, we discuss the identification and differentiation between overlapping ink and paint samples deposited on paper or fabric substrates. Raman mapping is used to differentiate between two paint samples that have virtually identical chemistry when analyzed via XPS, and rapid XPS imaging is used to identify the order of events between the deposition of computer-printed ink and handwritten ink from a ballpoint pen.

3:20pm **AS+EM+SE-TuA-4 Comparison of Methods to Quantify Silicone on Hair***, **Michaeleen Pacholski**, B. Johnson, T. Case, T. Powell, D. Carsten, J. Stratton,* The Dow Chemical Company*; C. Ji,* The Dow Chemical Company, China*; M. McIvor, N. Goodman, S. Yusuf, M. Upshur,* The Dow Chemical Company

Silicone has been used as a conditioning agent on hair for a long time.Silicone deposition can produce numerous benefits in reducing the coefficient of friction, improving combability and decreasing frizz.It can be delivered in multiple ways such as conditioning shampoo, rinse off conditioners, leave in conditioners and detangling products.Regardless of how it is delivered to the hair surface, the quantification of silicone on hair is an important metric for R&D product development and marketing.In a large analytical group there are many techniques that can be used including XPS, XRF, ICP, GC and IR.Each has different limits of detection, amount of sample required, time involved to both acquire and analyze the data, etc.A set of samples was generated using both shampoo and rinse off conditioner on both brown and bleached hair for a comparison study.The amount of silicone varied from low to high levels.Comparison of the techniques showed general agreement between all techniques within expectations.These experiments can now guide internal work based on the needs of the specific project and what instrumentation is available within that region.

4:20pm **AS+EM+SE-TuA-7 Progress Towards Atomic Scale Analytical Tomography***, **Brian Gorman**,* Colorado School of Mines*; T. Kelly,* Steam Instruments, Inc*; M. Holtz,* Colorado School of Mines **INVITED**

Atomic-Scale Analytical Tomography (ASAT) has been recently defined as the ability to identify every atom in its place. Specifically, ASAT is the ability to determine the isotopic identity and sub-Angstrom position of 100% of the atoms in a specific volume. Taking this a step further, ASAT should also be able to determine the local electronic structure of these atoms, thus giving rise to true 3-D atomic structure / electronic property relationships. ASAT datasets of semiconductor nanostructures will reveal the 3-D position of individual dopant atoms with pm spatial resolution, the 3-D position of nuclear spin isotopes, nanometer scale changes in strain due to structural defects and lattice mismatch, the 3-D position of point defects such as vacancies, and any electronic band structure changes at all these atomic-scale features.

Undoubtedly, ASAT is a lofty metrology goal but is nearly within reach. Contemporary metrology techniques such as (Scanning) Transmission Electron Microscopy ((S)TEM) are not currently capable of ASAT. (S)TEM can image atomic positions with better than 0.01 nm resolution in some specimens and tilt-series tomographic imaging can give 3-D information, sometimes at atomic resolution. Analytical STEM can be performed at atomic resolution in some cases, although identifying a single atom in 3-D is only possible in limited specimens and with poor depth resolution. Atom Probe Tomography (APT) can provide mass spectral information on individual atoms, however, 3-D image reconstruction methods are constrained by multiple empirical assumptions and lack of information about the specimen that limit the spatial resolution.

Recently, it was demonstrated that correlative TEM and APT on the same specimen can approach ASAT. We used (S)TEM imaging of the specimen before and after APT to define the analyzed 3-D volume. 4-D STEM diffraction was used to define atom positions within that volume (a dataset known as the specimen function) using information about the crystal space group, orientation, and lattice parameters. Individual isotopic nuclear spins are accurately placed within a semiconductor quantum do to within 0.05 Anstroms.

More work needs to be done using correlative TEM and APT to achieve ASAT, including demonstrating the ability to capture structural features such as interfaces and defects as well as 100% efficiency ion detectors. In the near future, ASAT will be achieved through integration of 100%

efficiency ion detectors, improved data handling algorithms, and integration of TEM and APT into a single instrument.

5:00pm **AS+EM+SE-TuA-9 Investigating 2d-Materials Using Correlative Spectroscopy & Microscopy***, **Tim Nunney**, R. Simpson, P. Mack, H. Tseng,* Thermo Fisher Scientific, UK

Across a wide range of application areas, understanding the chemistry and structure of surfaces and interfaces is crucial. In the last fifty years, X-ray photoelectron spectroscopy (XPS) has become established as a one of the key techniques for measuring surface and interface chemistry, and advances in instrumentation have enabled it to keep pace with the requirements for both academia and industry. XPS can deliver quantified surface chemistry measurements, and by using depth profiling, an understanding of layer and interfacial chemistry, but the limit on spatial resolution for XPS can prevent it from determining how the surface structure is related to the measured chemical properties. For example, how the changing morphology of the surface during a depth profile could influence the measured composition would be challenging to determine using just XPS.

Other experimental techniques which are unable to match the surface selectivity of XPS are able to provide complementary information to extend the data from XPS. Electron microscopy can provide high resolution imaging, with elemental composition provided by energy dispersive X-ray microanalysis, but without the same surface selectivity seen with XPS or Auger electron spectroscopy (AES). This can be a perfect complement to XPS analysis, so long as the same points of interest can be identified. Molecular spectroscopy, such as FTIR or Raman, can also provide complementary information to XPS, albeit with different sampling depths, which can be extremely useful to validate measurements or confirm particular molecular structures using the wide range of spectral libraries available for those techniques.

In this presentation, we will describe how a correlative approach using both surface analysis instrumentation and scanning electron microscopy can be used to characterize 2D nanomaterials. Samples of MoS_2 grown on Si substrates have been investigated using XPS, Raman and SEM to determine their composition and structure. To facilitate co-alignment of the analysis positions when moving between the instruments, special sample carriers and software alignment routines have been developed.

5:20pm **AS+EM+SE-TuA-10 Surface Analysis in Fujifilm Electronic Materials Research & Development Laboratory: Applications on Chemical Mechanical Planarization***, **Hong Piao**,* FUJIFILM Electronic materials USA., Inc.*; Y. Liang, K. Huang, B. Duong, J. McDonough, Y. Zhang, H. Lee, B. Hu,* FUJIFILM Electronic materials USA., Inc.

Chemical mechanical planarization (CMP) is a chemical reaction assisted polishing process in the semiconductor manufacturing industry. It has played a key role on integrated circuit (IC) manufacturing to anisotropically remove overburden material or specific layers in the film stacking and to planarize the topography at the wafer surface. Specific slurry formulations have been designed towards to the device structure and materials to be polished. The surface chemical processes at the interface of the wafer/slurry/pad have significant influence on the CMP performance. As device geometries are continuously shrinking as well as the introduction of new interconnect materials, the technological requirements on CMP performance have become more stringent. Thus, in-depth understanding of surface chemical processes which occur during polishing remains essential to the improvement of slurry design, the development of next-generation CMP processes and post-CMP cleaning applications.

Investigations aimed at understanding fundamental mechanisms usually employ electrochemical techniques. Surface analysis methods remain rather under-utilized in this field, especially when taking into account the explosive growth of these surface techniques for the analysis of “nano-structured” materials in other fields.Surface analysis tools (XPS, Tof-SIMS and AFM) at FUJIFILM Electronic Materials U.S.A., Inc. combined with other complementary testing methods have already shown great promise as a means of achieving fundamental knowledge to the mechanisms involved in CMP processes [1].

This review continues to highlight the promising role that surface chemical analysis methods can and should play in understanding the complex interplay that drives design of CMP slurry formulation for contributions to the CMP technology. Examples describing the CMP characterization have been given in several aspects that are growing in importance: (1) Cu, Co and Ru CMP, (2) Defects (organic residues,metal contaminants and particles) removal in a post-CMP cleaning process and (3) CMP consumables: root cause analysis of pad stains.

[1]Hong Piao, Yannan Liang, James McDonough, Tawei Lin, Hyosang Lee, Carl Ballesteros, Eric Turner, Abhudaya Mishra and Richard Wen, “*Industrial Applications of Surface Science in Chemical mechanical Planarization*”, The AVS 65th International Symposium, Oct. 21-26, 2018, Long Beach, California.

5:40pm **AS+EM+SE-TuA-11 Investigating GeTe as an Ovonic Threshold Switch with Spectroscopic and Electronic Techniques***, **Melissa Meyerson**, M. Kalaswad, M. King, D. Adams, J. Custer, P. Kotula, M. Rodriguez, S. Rosenberg,* Sandia National Laboratories

Ovonic threshold switches (OTS) are a class of two or three terminal devices that exhibit a sharp transition between resistive and conductive operating regions. This transition is temporary, with the device reverting to a resistive state once bias is de-asserted from the device. The volatile resistive behavior makes OTS devices very attractive as select devices for phase change memory, voltage controlled tunable filters, and other applications. Metal telluride thin films show unique temperature dependent characteristics that may make them good materials for OTS devices. In this study, we examine the effect of annealing temperature on the chemical, physical, and electronic properties of GeTe thin films including exploring changes in crystallinity, chemical composition, and switching behavior. More specifically, X-ray photoelectron spectroscopy shows a chemical transition that occurs between 125 °C and 150 °C that results in an increase in metallic Ge and decrease in metallic Te relative to the concentration of GeTe present. Similarly, X-ray diffraction shows a transition from amorphous to crystalline GeTe around 160 °C. The films are further characterized with transmission electron microscopy, energy dispersive X-ray spectroscopy, and surface electronic measurements including ultraviolet photoelectron spectroscopy and inverse photoelectron spectroscopy to determine the band gap.

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6:00pm **AS+EM+SE-TuA-12 Multi-Technique Analysis of Organic and Inorganic Semiconductors for Composition and Electronic Information***, **Paul Mack**,* Thermo Fisher Scientific, UK*; M. Modreanu,* Tyndall National Institute-University College Cork, Ireland

Photoelectron spectroscopy has been used for many years to analyse the elemental and chemical composition of a broad range of industrially relevant materials, from polymers to semiconductors.In recent years, with the development of novel organic and inorganic semiconductors, there has also been an increasing demand to measure electronic parameters alongside the elemental and chemical state information.

In this work, complementary electron spectroscopic techniques were used to comprehensively characterise organic and inorganic semiconductors for composition and electronic properties.X-ray photoelectron spectroscopy (XPS) was used to analyse the elemental and chemical composition of the organic semiconductor, P3HT, and a range of ferroelectric films with the general formula, $Hf_xZr_yO_z$.Ultraviolet photoelectron spectroscopy (UPS) and reflection electron energy loss spectroscopy (REELS) were then used together to measure the ionisation potential, band gap and electron affinities of those samples.

Chemical Analysis and Imaging Interfaces Focus Topic
Room 302 - Session CA+2D+AS+BI+HC+LS+NS-TuA

In Situ Microscopy, Spectroscopy and Processing at Liquid-Solid-Gas Interfaces

Moderators: Andrei Kolmakov, National Institute of Standards and Technology (NIST), **Xiao-Ying Yu**, Oak Ridge National Laboratory, USA

2:20pm **CA+2D+AS+BI+HC+LS+NS-TuA-1 Understanding Charge Carrier Variations on the Nanoscale Using Microwave Near-Field Microscopy***, **T. Mitch Wallis**, S. Berweger, P. Kabos,* National Institute of Standards and Technology **INVITED**

Understanding the spatial distributions of charge carriers and their polarity in nanoscale semiconductors and their devices remains a long-standing challenge. Scanning probe-based microwave impedance microscopy (MIM, also called scanning microwave microscopy, SMM) can directly probe charge-carriers on the nanoscale via the high-frequency capacitive interaction between the sharp tip and sample of interest.

Here we will first provide an overview of MIM, including applications to model systems. We will then focus on studies of active devices of semiconducting materials, including GaN nanowires and 2D crystals of elemental tellurium. We will conclude with an overview of recent efforts on photoconductivity mapping in 2D materials and hybrid organic-inorganic lead-halide perovskite thin films. In particular, for the latter we leverage the high bandwidth inherent in the microwave signal to obtain temporal resolution as high as 5 ns.

3:00pm **CA+2D+AS+BI+HC+LS+NS-TuA-3 Oxidation/Reduction of Cu Nanoparticles at a Single-Layer Graphene/Electrolyte Interface Monitored by Scanning Kelvin Probe Microscopy***, **Sidney Cohen**, S. Khatun, M. Andres, I. Pinkas, I. Kaplan-ashiri, O. Brontvein,* Weizmann Institute of Science, Israel*; I. Rosenhek-Goldian,* weizmann Institute of Science, Israel*; R. Weatherup,* Oxford University, UK*; B. Eren,* Weizmann Institute of Science, Israel

The need to probe chemical and physical processes occurring in at liquid/solid interfaces at small scales is being addressed by several cutting-edge techniques. Scanning probe microscopy (SPM) is now a well-established tool for simultaneous morphological, electrical, and mechanical characterization at the nanoscale. Scanning Kelvin Probe microscopy (SKPM) is an SPM method which can measure the work function at nm distance scales. This technique is not conveniently applied within a solution environment. In this work, micro-electrochemical cells were capped by a single layer graphene upper membrane which is transparent to the electrostatic field, enabling high resolution surface measurements of electrical processes occurring at the interfacial liquid region below the membrane. This talk will present this set-up, and show how it can be used to examine stability, and surface interactions in the oxidation/reduction processes of copper nanoparticles (NPs) attached to the graphene under operating (operando) conditions. Complementary techniques including cyclic voltammetry, and ex-situ electron microscopy and x-ray photoelectron spectroscopy gave a complete description of the processes. As an established catalyst for CO_2 reduction, the behavior of Cu in electrochemical conditions is of great interest in both science and technology. The measurements described here provided a nm-scale view of differences in Cu NP oxidation in ambient air and electrochemical conditions, detecting both a galvanic corrosion in air, and reversible reduction of the NPs at cathodic potentials in alkaline solution. Detachment of the NPs after long measurements of redox cycling is documented and rationalized.

3:20pm **CA+2D+AS+BI+HC+LS+NS-TuA-4 Investigation Tritium and Lithium transport along the Tritium-Producing Burnable Absorber Rod***, **Jiyoung Son**,* Pacific Northwest National Lab*; J. Gao,* PNNL*; G. Sevigny, S. Tripathi, B. Matthews,* Pacific Northwest National Lab*; X. Yu,* Oak Ridge National Laboratory

The compositional and microstructural changes in functional materials are critical for nuclear materials in fusion and fission applications. We investigated tritium (^{3}H) and lithium isotope (^{6}Li, ^{7}Li) transport within a neutron-irradiated target rod, aka, Tritium-Producing Burnable Absorber Rod (TPBAR), used in a light water reactor. TPBARs employ the iron aluminide-coated austenitic stainless-steel cladding and associated cruciform as key components. We used multimodal imaging tools and studied the specimens from irradiated TPBAR components. Specifically, a scanning electron microscope with focused ion beam (SEM-FIB) was used to prepare lift-out samples of the irradiated coating and cruciform samples for follow-up microanalysis. Time-of-flight secondary ion mass spectrometry (ToF-SIMS) was utilized to detect light isotopes in relation to tritium and lithium diffusion and transport. The observed distributions in the irradiated cladding specimens suggest light isotope mobility between internal target components as a result of neutron irradiation. We compared irradiated claddings of two different configurations in SIMS, and the chemical mapping and depth profiles of aluminide coatings show distinct light isotopic distributions. The cruciform specimens extracted from corresponding locations to the claddings also give interesting results. Overall, advanced correlative imaging results confirm tritium diffusion and lithium transport during the tritium production process. Such results give new insights into the fundamental transport mechanism within the target during irradiation and under non-equilibrium, extreme conditions.

4:20pm **CA+2D+AS+BI+HC+LS+NS-TuA-7 Development of a Workflow for Multiscale Elemental Analysis with X-ray Fluorescence Microscopy and Tomography***, **Si Chen**,* Argonne National Lab*; Y. Luo,* Argonne National Laboratory*; T. Paunesku,* Northwestern University*; O. Antipova, Y. Liu, N. Zaluzec, Z. Di,* Argonne National Laboratory*; G. Woloschak,* Northwestern University **INVITED**

Scanning X-ray fluorescence (XRF) microscopy and tomography provides powerful capabilities to assess the elemental distribution in a three-dimensional (3D) space and differentiate their inter- and intra-cellular interactions in complex biological cells and tissues. Like other microscopy techniques, there is often a tradeoff between spatial resolution and field-of-view that each XRF instrument can provide. For example, XRF nanoprobes are specialized for analysis with <50 nm resolution, but the region can be analyzed within a reasonable time frame is limited to only a few tens of microns. Therefore, the capability to combine the use of multiple instruments becomes important for hierarchical analysis.

In this presentation, we will discuss the Bionanoprobe (BNP) instrument and applications. The BNP is an XRF nanoprobe located at the Advanced Photon Source of Argonne National Laboratory. It is dedicated to the studies of biological tissues and cells with a subcellular spatial resolution. In conjunction with a microscale-resolution XRF instrument, we have demonstrated a workflow to perform multiscale elemental mapping and tomography on HeLa cells treated with non-targeted nanoparticles. While nanoscale tomography revealed the nanoparticle distribution in individual cells, statistical information on cell-nanoparticle interaction was obtained with the microprobe from a large population of cells.

It is important to note the challenges in sample preparation for such multiscale analysis across platforms. Different instruments often require different specimen dimensions in order to achieve their optimal performance. To enable analysis on the same specimen, we have introduced an intermediate specimen manipulation step between micro- and nano-scale measurements utilizing focused ion beam (FIB). Local regions of interest identified with the microprobe were isolated with a FIB instrument and further analyzed at the BNP. Angular enlargement for tomography data collection enabled by the FIB operation significantly improved the tomography reconstruction quality.

5:00pm **CA+2D+AS+BI+HC+LS+NS-TuA-9 in Situ Molecular Imaging of Green Solvents for CO_2 Capture***, **Xiao-Ying Yu**,* Oak Ridge National Laboratory, USA

Switchable ionic liquids are emerging green solvents in for carbon dioxide (CO_2) capture, cleaner separation, and efficient biomass production.However, the liquid structure and composition of SWILs are not fully understood.Besides off-line analyses using NMR and IR, our knowledge of the sustainable green solvents is limited.We used in situ liquid time-of-flight secondary ion mass spectrometry (ToF-SIMS) to study such solvents in this work.This is a unique in situ molecular imaging technique enabled by the invention of a vacuum compatible microfluidic reactor termed system for analysis at the liquid vacuum interface (SALVI).Green solvents of interest were synthesized and reported previously. They were introduced into the microfluidic channel for in situ analysis using liquid ToF-SIMS.Two model systems are illustrated in this talk.The first consists of 1, 8-diazabicycloundec-7-ene (DBU) and 1-hexanol with different CO_2 loadings.The second has koechanol with various CO_2 loadings.Koechanol acts as both acid and base in the latter.Our results show two coexisting liquid phases in these green solvents.This phenomenon was only hypothesized in previous theory prediction.We provide the first physical evidence of the complex liquid – liquid (l – l) interface using three-dimensional chemical mapping with submicrometer resolution.In addition, more complex stoichiometry is discovered due to CO_2 uptake.More importantly, we have provided the first chemical spatial visualization elucidating the evolving l – l interface.The more detailed molecular level understanding of the liquid structure and composition are instrumental to build the foundation for predicative material synthesis, CO_2 capture, and other versatile applications.

5:20pm **CA+2D+AS+BI+HC+LS+NS-TuA-10 Depth Dependence of Salt Ions at the Liquid/Vapor Interface Studied by Ambient Pressure X-Ray Photoelectron Spectroscopy***, A. Siebert, K. Goodman, **Monika Blum**,* LBNL

Liquid/vapor interfaces play an important role in chemical, biological, technological, and environmental processes. Perhaps one of the most important interfaces for the environment is the interface between atmospheric aqueous aerosols and the surrounding air, which affects reactions like the scattering and absorption of sunlight as well as the probability of aerosols to serve as cloud condensation nuclei. [1,2]

However, the experimental investigation of this active region is complicated by the necessary pressures far away from the ultra-high-vacuum (UHV) region, which is usually required in most surface science studies.[3]

In the recent past, ambient pressure X-ray photoelectron spectroscopy (APXPS) has proven to be a very powerful tool to study the chemical and electronic structure of liquids, solutions, and their interfaces with different media, not requiring the UHV conditions of standard XPS measurements. In this contribution we will utilize a colliding micro flat jet system with synchrotron-based APXPS to gain full insight into the depth dependency of different aqueous salt solutions, e.g. $CaCl_2$,at low salt concentrations. We will present a comparison of bulk ion concentrations in aqueous salt solutions and the surface ion concentration obtained from the ratio between the probed core level area and the peak area of the liquid water phase. This allows us to model the depth profile of salt ions in aqueous solutions and to correlate the data with existing theoretical models.

[1] Havala O. T. Pye et al., Atmos. Chem. Phys., 20, 4809–4888, 2020. [2] Barbara J. Finlayson-Pitts, Phys. Chem. Chem. Phys., 2009, 11, 7760–7779.

Spectroscopic Ellipsometry Focus Topic
Room 304 - Session EL1+AS+EM-TuA

Emerging Technological Advances and Breakthroughs of Spectroscopic Ellipsometry

Moderators: Alain Diebold, SUNY Polytechnic Institute, **Ruediger Schmidt-Grund**, Technical University Ilmenau, Germany

2:20pm **EL1+AS+EM-TuA-1 Terahertz to Vacuum Ultraviolet Ellipsometry Characterization of Spin, Lattice, Strain, Free Charge Carrier, Dielectric Constants, Exciton and Band-to-Band Transition Properties in Ultrawideband Gap Alpha and Beta Aluminum Gallium Oxide Semiconductor Alloys***, **Mathias Schubert**, R. Korlacki, M. Stokey,* University of Nebraska-Lincoln*; A. Mock,* Weber State University*; M. Hilfiker,* University of Nebraska-Lincoln*; J. Knudtson,* University of Nebraska-Lincoln, USA*; U. Kilic,* University of Nebraska-Lincoln*; S. Richter,* Lund University, Sweden*; S. Knight, P. Kuehne,* Linkoping University, Sweden*; V. Darakchieva,* Lund University, Sweden **INVITED**

Two phases of ultrawideband gap semiconductor gallium oxide emerge in composition with aluminum, the rhombohedral alpha and monoclinic beta phase of AlGaO. Progress in epitaxial deposition provides quality materials investigated currently with large efforts. Both phases permit access to ultrawideband gap properties reaching approximately 9 eV with sapphire. We employ a wide range of ellipsometry techniques covering 100 GHz to approximately 9.5 eV, including magnetic fields and density functional theory calculations. We provide an overview of current knowledge of properties for both compounds, discussing strain-stress relationships, evolution of phonon mode and band to band transition behaviors, dielectric constants, indices of refraction, anisotropy, and free charge carrier and defect properties [1-8]. We report on a new hyperbolic shear polariton formation in monoclinic Ga2O3 [9]. We also report on initial results of our newly developed instrumental approach for defect characterization in quantum materials, THz electron paramagnetic resonance ellipsometry for ultrahigh field and high resolution frequency spin detection and analysis in epitaxial semiconductor layer systems [10]. [1] M. Stokey et al., Phys. Rev. Materials 6, 014601 (2022). [2] M. Hilfiker et al., Appl. Phys. Lett. 118, 062103 (2021). [3] M. Hilfiker, U. Kilic, M. Stokey, R. Jinno, Y. Cho, H. Grace Xing, D. Jena, R. Korlacki, and M. Schubert, Appl. Phys. Lett. 119, 092103 (2021). [4] R. Korlacki, M. Stokey, A. Mock, S. Knight, A. Papamichail, V. Darakchieva, and M. Schubert, Phys. Rev. B 102, 180101(R) (2020). [5] P. Gopalan, S. Knight, A. Chanana, M. Stokey, P. Ranga, M. Scarpulla, S. Krishnamoorthy, V. Darakchieva, Z. Galazka, K. Irmscher, A. Fiedler, S. Blair, M. Schubert, and B. S. Rodriguez, Appl. Phys. Lett. 117, 252103 (2020). [6] M. Hilfiker, U. Kilic, A. Mock, V. Darakchieva, S. Knight, R. Korlacki, A. Mauze, Y. Zhang, J. Speck, and M. Schubert, Appl. Phys. Lett. 114, 231901 (2019). [7] J. A. Spencer, A. L. Mock, A. G. Jacobs, M. Schubert, Y. Zhang, and M. J. Tadjer, Appl. Phys. Rev. 9, 011315 (2022). [8] R. Korlacki, J. Knudtson, M. Stokey, M. J. Hilfiker, V. Darakchieva, and M. Schubert, Appl. Phys. Lett. 120, 042103 (2022). [9] N. Passler, X. Ni, G. Hu, J. R. Matson, M. Wolf, M. Schubert, A. Alù, J. D. Caldwell, T. G. Folland, and A. Paarmann, Nature 602, 595 (2022). [10] M. Schubert, S. Knight, S. Richter, P. Kuehne, V. Stanishev, A. Ruder, M. Stokey, R. Korlacki, K. Irmscher, P. Neugebauer, and V. Darakchieva, Appl. Phys. Lett. 120, 102101 (2022).

Spectroscopic Ellipsometry Focus Topic
Room 304 - Session EL2+EM-TuA

Spectroscopic Ellipsometry: Novel Applications and Theoretical Approaches

Moderators: Alain Diebold, SUNY Polytechnic Institute, **Ruediger Schmidt-Grund**, Technical University Ilmenau, Germany

4:20pm **EL2+EM-TuA-7 A Study of Wire Grid Polarizers with Mueller Matrix Ellipsometry***, T. Gholian Avval, M. Linford,* Brigham Young University*; N. Keller, **G. Andrew Antonelli**,* Onto Innovation, Inc.

Wire grid polarizers are essential optical components used in a wide variety of optical systems, from AR/VR to medical imaging to optical measuring systems. Physical properties of the polarizer, such as groove height and width all impact the polarizer's efficiency. Here we show how a wire grid polarizer can be characterized non-destructively in the fabrication process with Mueller Matrix ellipsometry and RCWA-based analysis. Using this methodology, physical properties like grating profile, height, pitch, material thicknesses and even grating tilt can be measured non-destructively and inline to provide process control.

4:40pm **EL2+EM-TuA-8 Temperature Dependence of the Direct Band Gap of InSb from 80 to 700 K***, **Melissa Rivero Arias**, N. S. Samarasingha, C. Emminger, S. Zollner,* New Mexico State University

In this undergraduate student presentation, we describe measurements of the dielectric function of bulk InSb near the direct band gap using Fourier-transform infrared (FTIR) spectroscopic ellipsometry from 80 to 800 K in an ultra-high vacuum (UHV) cryostat with diamond windows. Indium antimonide (InSb) is the zinc blende compound semiconductor with the smallest direct band gap (ε_0= 0.18 eV at room temperature) due to its heavy elements and the large resulting spin-orbit splitting and Darwin shifts. It also has a low melting point of 800 K. Previously, the bandgap of InSb has mostly been measured optically up to room temperature and estimated from Hall effect measurements of the effective mass up to 470 K. Ellipsometry measurements of the direct gap of InSb have been described at 300 K. Calculations indicate that InSb should undergo a topological phase transition from semiconductor to semi-metal (and topological insulator) at 600 K. It is interesting to see in the data if this transition occurs below the melting point of InSb.

5:00pm **EL2+EM-TuA-9 Coherent Acoustic Phonon Oscillations in Ge Using Pump-Pulse Time-Resolved Spectroscopic Ellipsometry***, **Carlos Armenta**,* New Mexico State University*; M. Zahradnik,* ELI Beamlines, Czechia*; C. Emminger,* Humboldt University Berlin, Germany*; S. Espinoza, M. Rebarz, J. Andreasson,* ELI Beamlines, Czechia*; S. Zollner,* New Mexico State University

Photoexcitation of bulk materials can create hot charge carriers that relax by transferring energy to the lattice, hence exciting phonons in the process. By photoexciting the material through femtosecond laser pulses, coherent acoustic phonon (CAP) oscillations at picosecond time scales are generated via this method. These CAP oscillations are related to an increase in charge carrier density, as well as strain triggered by the laser pulse, however details of this relationship are scarce in the literature. CAP oscillations affect the pseudo-dielectric function (DF) of the material, which makes time-resolved spectroscopic ellipsometry ideal to understand the processes in hand.

The present work aims to describe the relationship between CAP oscillations and charge carrier density, as well as surface orientation dependence via femtosecond pump-probe ellipsometry of Ge. Photoexcitation is induced by 800 nm laser pump pulses at different intensities, generating a strain pulse that travels normal to the surface within the ~200 nm penetration depth in the semiconductor. Measurements in Ge at (100), (110), and (111) orientations and charge carrier concentrations ranging from $\sim 7.5\times10^{20}$ cm^{-3} to $\sim 3.5\times10^{21}$ cm^{-3} were performed. The behavior of these oscillations is characterized by analyzing the changes in the pseudo-DF of Ge as a function of the delay time between the pump and probe pulse. Analyzing the E1 and E1+Δ1 critical points (CP) and the variation of their parameters (energy, broadening, amplitude, and phase) with delay time, the behavior of phonon oscillations can be studied.

In order to determine these parameters, second derivatives of the pseudo-DF were calculated using a linear filter technique based on extended Gauss (EG) functions. The periods of these oscillations are deduced by tracking the energy of these CPs as a function of time

5:20pm **EL2+EM-TuA-10 Time-Resolved Spectroscopic Ellipsometry Helped by Imaging Spectroscopic Ellipsometry***, **Shirly Espinoza**,* ELI Beamlines, Czechia

Thanks to femtosecond pulsed lasers, at ELI Beamlines in the Czech Republic, we developed a time-resolved femtosecond ellipsometry technique, where a pump beam from any wavelength between 200 nm and 2000 nm excites a material; and a second pulse, the probe beam, with a continuous spectrum from 350 nm to 750 nm measures the dielectric function of that material. The pump and the probe beam can be separated in time from femtoseconds to nanoseconds generating a time-scan of the relaxation processes that happens in the material when it returns to its original unexcited state.

This time-resolved pump-probe ellipsometry technique is available to the scientific community through a yearly call for user proposals. We then get the opportunity to measure different type of materials from thin films to crystals of semiconductors and metals including 2D materials and organic samples deposited on metal layers. By imaging ellipsometry, the sample inhomogeneity, roughness and optical properties prior and after the pump-probe measurement are diagnosed. A discussion about newly imaging-analyzed samples that were and will be study by pump-probe ellipsometry will be presented.

Fundamental Discoveries in Heterogeneous Catalysis Focus Topic
Room 321 - Session HC+AS+SS-TuA

Bridging Gaps I: Structural and Dynamic Effects in Catalysis

Moderator: Dan Killelea, Loyola University Chicago

2:20pm **HC+AS+SS-TuA-1 Fundamental Studies of C1 Catalysis on Metal-oxide and Metal-Carbide Interfaces***, **Jose Rodriguez**,* Brookhaven National Laboratory **INVITED**

The transformation of CO_2 and CH_4 into alcohols or other hydrocarbon compounds is challenging because of the difficulties associated with the chemical activation of this highly stable molecules by heterogeneous catalysts. Pure metals and bimetallic systems used for this task have usually trouble binding CO_2 or CH_4 and, thus, low catalytic activity. Here, we will discuss a series of in-situ studies investigating different mechanisms or approaches for C-O and C-H bond activation. They illustrate the advantages of metal-oxide and metal-carbide interfaces when aiming at the conversion of CO_2 or CH_4 into methanol. CeOx/Cu(111), Cu/CeOx/TiO_2(110) and Cu/TiC(001) exhibit an activity for the $CO_2 \rightarrow CH_3OH$ conversion that is 2-3 orders of magnitude higher than that of a benchmark Cu(111) catalyst. In the Cu-ceria and Cu-TiC interfaces, the combination of metal and oxide (or carbide) centers affords complementary chemical properties that lead to special reaction pathways for methanol synthesis. Metal-oxide and metal-carbide interfaces also can be tune for the activation and conversion of CH_4.

3:00pm **HC+AS+SS-TuA-3 Atomic Scale Studies of Chromium Species on Iron Oxide Surfaces***, **Moritz Eder**,* TU Wien, Austria*; P. Sombut,* University of Vienna, Austria*; C. Wang, L. Puntscher, A. Rafsanjani-Abbasi, M. Meier, J. Pavelec, G. Franceschi, M. Riva,* TU Wien, Austria*; C. Franchini,* University of Vienna, Austria*; M. Schmid, U. Diebold, G. Parkinson,* TU Wien, Austria

Chromium (Cr) ferrite catalysts are industrially employed for the water gas shift reaction in order to provide large amounts of molecular hydrogen.[1] However, the European REACH legislation demands that hexavalent Cr be banned from all catalysts used in industrial processes due to its toxicity. Consequently, alternative metals are sought to fulfill the role of Cr species in the corresponding compounds.[2] It is therefore necessary to obtain a fundamental understanding and characterization of Cr on iron oxides.

In this talk, we present the investigation of Cr species on Fe_3O_4(001) by means of STM and XPS at room temperature. We show the behavior during exposure to water gas shift reactants (i.e., CO and H_2O) and upon high temperature treatment. The latter is of utmost importance since the water gas shift reaction is conducted at temperatures up to 500°C.[1] The results are compared to the behavior of other transition metals and discussed with respect to implications for applied catalysis.[3]

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[2] Glassner, *Int. Surf. Technol.***14**, p. 36, (2021)

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3:20pm **HC+AS+SS-TuA-4 Investigation of CO Oxidation on Oxygenated Rh(111) Surfaces with RAIRS***, **Elizabeth Jamka**, D. Killelea,* Loyola University Chicago

Surface IR spectroscopy is a quantitative technique that also provides information about the binding sites and chemical environments of the adsorbed CO molecules. In this research we are able to interface a FTIR to the ultra-high vacuum (UHV) chamber as a non-destructive and highly sensitive surface analysis technique. Because IR measurements can be performed in UHV conditions, interference from atmospheric species are avoided, while enabling investigation of catalytic systems, like carbon monoxide (CO) to carbon dioxide (CO_2) on Rh(111). To determine the reactivity of the various oxide phases, the oxidation reaction of CO to CO_2 on oxidized Rhodium (Rh) will be utilized as a probe reaction. Studying CO oxidation on different Rh surfaces will provide atomic level information regarding oxidation reactions, progressing the understanding of various surface phases relevant to many Rh catalyzed processes. This research focuses on CO sticked to clean Rh(111), (2x1)-O/Rh(111), and (2x1)-O + RhO_2/Rh(111). Via FTIR, these and other reaction sites of CO oxidation will be investigated to determine reaction pathways or mechanisms.

4:20pm **HC+AS+SS-TuA-7 Molecular Beam Surface Reaction Experiments with Chiral Molecules***, **Tim Schäfer**,* Georg August University, Goettingen, Germany **INVITED**

Chirality is a feature of asymmetry describing the geometrical property of objects that cannot be mapped onto their mirror images like our hands as classic example. In chemistry, one observes chirality on the molecular level: two mirror images of chiral molecules (enantiomers) have only little difference in the structure, but this might cause a vast change in the biological activity.

Unfortunately, a fundamental understanding of chemical processes in chiral environments is challenging, as enantiosensitive detection methods must introduce chirality to distinguish enantiomers. Until recently, enantiospecific assignment of chiral gas phase molecules at low concentrations was not even possible. In the last decade, new enantiosensitive detection techniques have been invented based on photoionization of molecules (Photoelectron Circular Dichroism, PECD). Our group contributed to these advances by developing a unique technique that combines PECD with surface science. This approach allows the investigation of dynamics and kinetics of surface reactions of chiral molecules at the gas surface interface.

We use this technique for studies on heterogeneously catalyzed chiral surface reactions like the partial oxidation of olefins to epoxides on metal surfaces. For this, we combine PECD measurements with velocity resolved kinetics experiments, providing enantiosensitive information about reaction mechanisms at surfaces.

5:00pm **HC+AS+SS-TuA-9 A Local View on the Influence of Solvent and Product on the Reactivity of Surface-Catalyzed Reactions***, **Karina Morgenstern**,* Ruhr Universität Bochum, Germany **INVITED**

Though largely influencing the efficiency of a reaction, the molecular-scale details of the local environment of the reactants are experimentally inaccessible hindering an in-depth understanding of a catalyst's reactivity, a prerequisite to maximizing its efficiency. We introduce a method to follow individual molecules and their largely changing environment during laser-induced reactions. The method is illustrated with a single-molecule resolution on two examples, the dissociation of halogenated benzene molecules adsorbed on ice [1] and of CO_2 on two catalytically relevant surfaces, Ag(100) and Cu(111)[2]. Dissociation of halobenzene is triggered by delocalized excess electrons. The adsorption on ice sufficiently lowers the energy barrier for the transfer between themolecular orbitals to facilitate dissociation of bromo- and chloro- but not of fluorobenzene at cryogenic temperatures.For the CO_2dissociation, we reveal how the reactant's surroundings evolve with progressing laser illumination and with it their propensity for dissociation. Our results shed light on the influence of solvent and products on reaction yields on the nanoscale.

[1]P. Auburger, I. Kemeny, C. Bertram, M. Lingges, M. Bockstedte, U. Bovensiepen, K. Morgenstern, Phys. Rev. Lett. 121, 206001 (2018)

[2] M. Vyshnepolsky, Z.-B. Ding, P. Srivastava, P. Tesarik, H. Mazhar, M. Maestri, K. Morgenstern, Angew. Chem. Int. Ed. 60, 18217-18222 (2021)

5:40pm **HC+AS+SS-TuA-11 Enhanced Catalytic Selectivity Due to Topographically Reduced Work Function of Carbon Nanospikes***, **Arthur P. Baddorf**,* Center for Nanophase Materials Sciences, Oak Ridge National Laboratory*; A. Rondinone,* Center for Integrated Nanotechnologies, Los Alamos National Laboratory*; D. Hensley,* Center for Nanophase Materials Sciences, Oak Ridge National Laboratory

Carbon nanospikes show excellent Faradaic efficiency and selectivity for electrochemical conversion of technologically important reactions, including CO_2 to ethanol in the presence of Cu [1] and N_2 to ammonia in the presence of Li [2]. Rates are higher than for other aqueous electrochemical approaches, including other low-dimensional carbon nanomaterials such as nanotubes, fibers, and foams, and much greater than for flat carbon surfaces. The essential attribute appears to be the sharp spike topography at which electric fields are enhanced. Transmission electron microscopy images reveal that films consist of a high density of nanospikes each 50-80 nm in height and terminated with a sharp tip of radius ~1 nm, i.e. a very high curvature.

We have explored the electric fields at the nanospikes by measurements of the absolute work function in comparison that of other carbon geometries using ultraviolet photoemission spectroscopy (UPS). As samples were characterized after transfer through air, surface cleanliness was monitored with x-ray photoelectron spectroscopy (XPS). Annealing as-grown samples above 275 °C was required to produce a clean surface which has a 4.13 eV work function, a half volt lower than that of flat graphite. This reduction supports the idea that a strong electric field is generated by the nanospike topography which contributes to the electrochemical activity.

Contamination of the spiked surface raises the work function above that of the clean nanospikes. Work function values following exposure increased to 4.19 eV for hydrocarbons, 4.30 for air, 4.42 for water, and 4.48 for oxygen. Blunting the spikes, by exposure to an oxygen plasma, argon sputtering, or annealing to 800 °C results in a work function close to that of flat graphite, 4.62 eV. An unusual double onset in the UPS secondary electron intensity is observed after absorbing hydrocarbons on clean nanospikes. This double onset has not been reported on metal surfaces and appears to be unique to carbon substrates. The energy difference between the two onsets, about 0.4 eV is close to that of a typical C-H stretch in hydrocarbons suggesting the lower energy onset may originate in inelastic scattering of photoelectrons.

* This work was supported by Center for Nanophase Materials Sciences (CNMS), which is a US Department of Energy, Office of Science User Facility at Oak Ridge National Laboratory.

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6:00pm **HC+AS+SS-TuA-12 HC Graduate Student Finalist Talk: Enhanced Descriptor Identification and Mechanic Understanding for Catalytic Activity using Data-Driven Framework: A Case Study of CO Hydrogenation over Cu-Based Single Atom Alloys***, **Wenjie Liao**,* Stony Brook University/Brookhaven National Laboratory*; P. Liu,* Brookhaven National Laboratory and State University of New York at Stony Brook

Accurate identification of descriptors for catalytic activities has long been essential to the in-depth mechanic study of catalysis and recently to set the basis for catalyst screening. However, commonly used derivative-based local sensitivity analysis methods suffer from low accuracy in predictability. This study reports an enhanced approach to accurately identifying the descriptors from a kinetic dataset using the machine learning (ML) surrogate model. The CO hydrogenation to methanol over Cu-based single atom alloys was taken as a case study.

Our model captures not only the contribution from individual elementary steps (i.e., first-order descriptors), but also the interaction between relevant steps within a reaction network (i.e., second-order descriptors), which was found to be essential for accuracy. As a result, six effective descriptors are identified, which are accurate enough to ensure the trained gradient boosted regression (GBR) model for well prediction of the methanol turn-over-frequency (TOF) over metal (M)-doped Cu(111) model surfaces (M = Au, Cu, Pd, Pt, Ni). More importantly, going beyond the purely mathematic ML model, the catalytic role of each identified descriptor can be revealed by using the model-agnostic interpretation tools, which enhances the mechanic insight into the promoting effect of alloying. The trained GBR model outperforms the conventional derivative-based methods in terms of both predictability and mechanic understanding.

The proposed data-driven framework allows one to identify key descriptors beyond rate-limiting steps while clearly depicting how each identified key descriptor would affect the catalytic activity when more than one activation energies were tuned. This approach can be applied to other reactions and catalysts, which opens alternative possibilities toward accurate descriptor-based rational catalyst optimization

New Trends on Structural and Electronic Characterization of Materials, Interfaces, and Surfaces Using Synchrotron and FEL-Based Radiation Sources Focus Topic
Room 318 - Session LS1+2D+AS+EM+QS+SS-TuA

Operando Catalysis and Energy Systems

Moderator: Jyoti Katoch, Carnegie Mellon University

2:20pm **LS1+2D+AS+EM+QS+SS-TuA-1 In-situ/Real-time XPS Study of Electrochemical Reactions in All-solid-state Thin-film Lithium-Ion Batteries***, **Takuya Masuda**,* National Institute for Materials Science, Japan **INVITED**

All-solid-state lithium-ion batteries (ASSLIBs) are one of the most promising next generation rechargeable batteries because of their very high safety and reliability. Understanding of the mechanism of electrochemical reactions and related physicochemical phenomena is very important for improving cell performances and durability. Application of ex-situ techniques to multiple samples disassembled from cells after certain charge/discharge cycles often results in misinterpretation due to the variation of samples and undesired side effects during sample transfer between battery test environment and characterization apparatus. Thus, various in-situ techniques which can be applied to the same position of the same sample kept at a certain charge/discharge state have been developed for hierarchical understanding of a series of electrochemical events interplaying with each other. X-ray photoelectron spectroscopy (XPS) is a powerful tool for analyzing the composition of reaction products, chemical state, and electronic structure of sample surfaces. By tuning the energy of incident x-rays, it also enables us to conduct the depth-resolved analysis of surfaces and interfaces including those buried with solid thin films. Recently, we developed an in-situ XPS apparatus equipped with a bias application system and a vacuum suitcase for sample transfer,[1] and applied it to the electrochemical lithiation/delithiation reactions of an amorphous Si thin film electrode sputter-deposited on a solid electrolyte sheet.[2] The chemical state of Si electrode changing during lithiation/delithiation processes was successfully tracked by sequential XPS measurements in the regions of Li 1s, C 1s, O 1s, and Si 2p. Not only lithium silicide (Li_xSi) which reversibly responds to the lithiation/delithiation but also irreversible species such as lithium oxides, lithium silicates and lithium carbonates were formed due to the lithiation of the Si electrode. Moreover, a rapid spectral change attributable to the phase transition of a crystalline Li_xSi to an amorphous phase was observed in the successive delithiation after preceding lithiation up to certain level. Based on the state of charge, Li content x in Li_xSi, and positions of XPS peaks, we summarized the lithiation/delithiation mechanism in Si electrodes. Further details will be presented.

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3:00pm **LS1+2D+AS+EM+QS+SS-TuA-3 Interaction of Molecular Nitrogen with Vanadium Oxide in the Absence and Presence of Water Vapor at Room Temperature: Near-Ambient Pressure XPS***, S. Nemsak,* Lawrence Berkeley National Laboratory*; **Kabirat Balogun**, P. Chukwunenye, T. Cundari, P. Bagus, J. Kelber,* Department of Chemistry, University of North Texas

Interactions of N_2 and H_2O at transition metal oxide surfaces are of fundamental interest for gaining insight into electrocatalytic nitrogen reduction reaction (NRR) mechanisms. N_2/H_2O interactions at the polycrystalline vanadium oxide/vapor interface were monitored at room temperature and N_2 partial pressures between 10^{-9} Torr and 10^{-1} Torr using

Near-Ambient Pressure X-ray Photoelectron Spectroscopy (NAP-XPS). The oxide film was predominantly V(IV), with significant V(III) and V(V) components. Such films have been previously demonstrated to be NRR active at pH 7. There is little understanding, however, of the detailed nature of N_2-surface interactions. XPS measurements were acquired at room temperature in environments of both pure N_2 and equal pressures of N_2 and H_2O vapor, up to a N_2 partial pressure of 10^{-1} Torr. In the absence of H_2O, broad N 1s features were observed at binding energies of 401 eV and 398.7 eV with relative intensity ratios of ~ 3:1, respectively. These features remained upon subsequent pumpdown to 10^{-9} Torr, indicating that adsorbed nitrogen is stable at room temperature in the absence of equilibrium with gas phase N_2. In the presence of equal pressures of N_2 and H_2O vapor, the 401 eV N 1s feature was reduced in intensity by ~ 50% at 10^{-1} Torr N_2 partial pressure, with the feature at 398.7 eV binding energy barely observable. DFT calculations show that the above NAP-XPS data demonstrating stable N_2-surface binding in the absence of N_2 overpressure are consistent with N_2 binding at V(IV) or V(III) sites, but not at V(V) sites, and further show that N_2/H_2O binding is competitive. SCF-HF calculations suggest that the two N 1s XPS features correspond to "shake" and normal transitions at 401 eV and 398.7 eV, respectively, for N_2 bonded end-on to the surface. The shake feature involves a charge transfer from V 3d to N_2 pi* in addition to N 1s ionization. The difference in binding energies of the two features, ~ 2.3 eV, strongly suggests N_2 -V(III) binding. The data presented demonstrate the ability of NAP-XPS, in concert with theory, to provide atomic-level insight concerning interfacial reactions relevant to electrocatalysis.

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3:20pm **LS1+2D+AS+EM+QS+SS-TuA-4 Catalysts Caught in the Act: an Operando Investigation of Copper during CO_2 Hydrogenation**, ***Elizabeth Jones,*** University of Oxford, UK

Amongst the foremost challenges in mitigating global warming are replacing fossil fuels with renewable alternatives, and storing/using carbon captured from CO2-emitting processes. Methanol production by CO2 hydrogenation promises a possible solution to both of these issues, particularly if H2 can be obtained through water electrolysis. When the resulting methanol is used as a fuel an equivalent amount of CO2 is released making it a “net-zero” fuel alternative. CO2 hydrogenation is performed industrially using a CO2/H2 mix at 200-300oC, 50-100 bar with a Cu-based catalyst, and the addition of CO is known to increase the methanol yield. However, mechanistic understand of this reaction and the role played by CO remains limited. Soft X-ray spectroscopies can provide details on the chemical state of copper to uncover the chemistry behind this reaction, however the typical requirement for measurement under high vacuum constrains how realistic these studies can be. There has been much recent development on improving operando techniques to enable heterogeneous catalytic reactions to be studied under realistic pressure conditions (E. S. Jones et al., in Ambient Pressure Spectroscopy in Complex Chemical Environments, 2021, ACS Symposium Series, vol. 1396, ch. 8, 175-218). A promising approach is to use an environmental cell which encloses the desired gas and separates it from the high vacuum environment, using an X-ray transparent window (R. S. Weatherup, J. Phys. Chem. Lett., 2016, 7, 1622-1627).

Using a custom-designed high pressure environmental cell we have studied model Cu catalysts using operando NEXAFS in total electron yield mode up to pressures of 1 bar and temperatures of 200oC. A thin Cu film was deposited onto a Si3N-4 membrane which acted to seal the high pressure gas within the cell and as a transparent window for incident X-rays. The aim of the study was to investigate how the Cu oxidation states varied when exposed to H2 and CO2 in different sequential order and how the introduction of CO can further influence the chemical state of Cu. It was found that H2 can provide a protective barrier to oxidation from CO2 when dosed first, however if H2 was added after CO2 it is unable to return the surface to its metallic state where CO is then required for reduction. This offers an insight into why CO plays an important role in the industrial production of methanol. Additionally, advances in sealing of the environmental cell enabled high pressures to be achieved at elevated temperatures, allowing this approach to be extended to more industrially-relevant conditions.

New Trends on Structural and Electronic Characterization of Materials, Interfaces, and Surfaces Using Synchrotron and FEL-Based Radiation Sources Focus Topic
Room 318 - Session LS2+2D+AS+TF-TuA

Role of Defects in Materials

Moderator: Takuya Masuda, National Institute for Materials Science, Japan

4:20pm **LS2+2D+AS+TF-TuA-7 Visualizing Complex Many-Body Phenomena in 2D Materials Based Heterostructures and Devices*, Jyoti Katoch,*** Carnegie Mellon University **INVITED**

Two-dimensional (2D) materials offer the freedom to create novel condensed matter systems, with unique properties, by mechanically assembling different (or same) 2D materials layer-by-layer to form atomically sharp vertical or lateral heterostructures. The van der Waals (vdW) heterostructures with small lattice mismatch and a relatively small twist angle between the constituent layers, have shown to exhibit coexisting complex phases of matter including Mott insulating state, superconductivity, bound quasiparticles, and topological states. The advent of the state-of-the-art angle-resolved photoemission spectroscopy with high spatial resolution (micro- and nano-ARPES) and the ability to perform these measurements on fully functional devices, has made it possible to directly probe many exotic physical phenomena in 2D based material systems. In this talk, I will discuss the utilization of the nanoARPES to investigate the highly tunable many-body effects in 2D based heterostructures and their devices.

5:00pm **LS2+2D+AS+TF-TuA-9 Dynamic Grating Development for Neutron Imaging Across Multiple Length Scales*, Sarah M. Robinson,*** *R. Murphy, J. LaManna, C. Wolf,* National Institute of Standards and Technology (NIST)*; Y. Kim, M. Daugherty,* National Institute of Standards and Technology (NIST)/ University of Maryland, College Park*; M. Huber, P. Bajcsy, P. Kienzle, K. Weigandt, D. Hussey, N. Klimov,* National Institute of Standards and Technology (NIST)

Current neutron scattering techniques can provide sample structural information on the length scales of nano- to micrometers, but it is challenging to investigate the hierarchical structures found in non-homogeneous samples. We are developing a far-field grating interferometer (INFER) to nondestructively study the microstructures of samples averaged over a voxel size of 50 µm. In order to perform far-field neutron interferometry across multiple length scales, a large number of source grating periods are used to multiplex the signal and impart the required transverse quasi-coherence. To eliminate the need of fabricating, installing, and aligning a new static source grating for each period, we have developed a DynAmic ReconfIgUrable Source grating (DARIUS). DARIUS is a wafer-scale silicon microfluidic device that allows for the real-time adjustment of the grating period, ranging from 20 µm to 20,000 µm, with the potential to replace more than 500 static source gratings. In DARIUS, each of 5,000+ individual grating channels can be selectively infilled with a neutron and x-ray absorbing fluid to modulate the neutrons, creating an absorbing grating with an effective period based on the locations of the opaque fluid. A key part of DARIUS is a diffraction grating layer fabricated on a 100 mm Si wafer. In this layer, the grating channels are etched in silicon with period of 20 µm and depth of 125 µm, corresponding to a channel volume of enough fluid to locally attenuate the neutron beam. We have previously demonstrated that we can selectively fill 128 active channels with x-ray absorbing solution and, with that, modulate in real time an x-ray beam. Our next prototype, DARIUS-2.0, has an active area of 40.96 mm x 51.20 mm with 2,560 active channels on a single side of a 100 mm Si wafer. The channels are sealed by wafer-scale eutectic bonding to a capping wafer with vias for well and pumping port access. We will present results on initial testing of DARIUS-2.0 with x-ray imaging and progress on scaling up to a double-sided grating device to be incorporated in INFER to unlock the ability of analysis over a wider range of length scales.

5:20pm **LS2+2D+AS+TF-TuA-10 Dynamics, Stability and History-Dependence of Magnetic Skyrmions in the 2D van der Waals Magnets Fe_xGeTe_2**, ***Kai Litzius***, *M. Birch, L. Powalla, S. Wintz,* Max Plank Institute for Intelligent Systems, Germany*; M. Weigand,* 4Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Germany*; K. Kern, M. Burghard, G. Schutz,* Max Plank Institute for Intelligent Systems, Germany **INVITED**

Recently, the combination of 2-dimensional (2D) magnetism [1] with the field of spintronics, i.e. the manipulation of magnetic states with electric currents, has started to gain much traction in modern solid-state physics. The prospect of highly efficient low-dimensional devices, extreme ease to fabricate versatile heterostructures by stacking of separate individual layers, and the report of chiral topological magnetic solitons in 2D itinerant ferromagnets have further enhanced the field's interest in this fascinating class of materials. Requirements for technological implementation, however, are generally to realize both the fabrication of nanoscale devices and to understand different potential ways to tailor the material parameters and ferromagnetic ordering temperatures [2,3] in desirable ways.

In this work, we utilize real-space imaging of the magnetic texture in thin flakes of the van der Waals magnets Fe_xGeTe_2 to determine magnetic phase diagrams of various exfoliated films with varying compositions. We furthermore realize devices for local injection of skyrmions by means of vertical nanocontacts. Our findings show besides complex, history-dependent magnetization states also that changes in the composition and crystalline structure significantly alter the magnetic behavior and may be used to tune the stability of skyrmions or other magnetic textures in these novel magnetic systems. Ultimately, the choice of composition and nucleation mechanism result in a selective stabilization of a variety of (meta-) stable magnetic configurations. Especially individual skyrmions can then be injected by targeted current pulses through a nanocontact. Our findings open novel perspectives for designing van der Waal heterostructure-based devices incorporating topological spin textures.

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Magnetic Interfaces and Nanostructures Division
Room 330 - Session MI-TuA

Topological Insulator Heterostructures

Moderators: Axel Enders, University of Nebraska-Lincoln, Germany, **Valeria Lauter**, Oak Ridge National Laboratory

2:20pm **MI-TuA-1 Evidence of Antiferromagnetic Coupling between Topological and Magnetic Insulators***, **Leonid Rokhinson**,* Purdue University **INVITED**

Exchange interaction between topological and magnetic insulators enables local control of topologically protected surface states by lithographically shaping magnetic materials. In previous works ferromagnetic exchange has been successfully realized. We report an experimental evidence of antiferromagnetic exchange between a topological insulator Bi2Se3 and a magnetic insulator EuSe. Spin-polarized neutron reflectometry reveals reduction of in-plane magnetic susceptibility up to 25K, well above the Neel temperature of the bulk EuSe. A combination of SQUID magnetometry and transport measurements indicates an antiferromagnetic interfacial exchange coupling that opens an energy gap in topological surface states. High temperature local control of topological surface states with zero net magnetization opens new opportunities for the design of electronic, spintronic and quantum computation devices, ranging from quantization of Hall conductance at zero fields to spatial localization of non-Abelian excitations in superconducting topological qubits.

3:00pm **MI-TuA-3 Infrared Magnetospectroscopy of Magnetic Topological Insulator Heterostructures***, **Badih Assaf**,* University of Notre Dame **INVITED**

Topological insulator (TI)-magnetic insulator(MI) heterostructures are employed to achieve efficient electrical switching of magnetization, owing to the spin-charge coupling enabled by the helical Dirac surface states of the TI. These surface states are however prone to the breaking of time-reversal symmetry by magnetism. A magnetic insulator deposited on the surface of a TI is thus hypothesized to induce a gapping of the Dirac surface states. This energy gap is challenging to measure using common surface spectroscopies since the surface is buried under the magnetic insulator. We develop TI-MI heterostructures based on the topological crystalline insulator $Pb_{1-x}Sn_xSe$ (x>0.2) and a magnetic insulator EuSe. The high mobility achieved in PbSnSe (>10000cm^2/Vs) allows us to measure the magnetic proximity induced gap using magnetooptical Landau level spectroscopy up to 17.5T at 4.5K. We find the upper bound of this gap to be close to 20meV. We confirm the coexistence of this gapped Dirac state with magnetism using neutron reflectometry. This result has important implications on the potential of TCIs for devices that rely on proximity between a magnet and a topological material, such as spintronic switching devices, since it is evident that the gap remains smaller than the Fermi energy and likely should not influence the spin-charge coupling characteristics of the TI.

4:20pm **MI-TuA-7 Topological States in the van der Waals Magnet $MnBi_2Te_4$: from 3D to 2D***, **Hendrik Bentmann**,* Wuerzburg University, Germany **INVITED**

The interplay of topology and magnetism is a route to spintronic applications based on dissipationless charge and spin transport. The van der Waals material MnBi2Te4 naturally combines strong spin-orbit interaction and local magnetic moments, opening a playground for the study of magnetic topological phenomena. In its 3D bulk phase, MnBi2Te4 forms an antiferromagnetic topological insulator [1]. Related topological states are also realized in the modular modular (Bi2Te3)n(MnBi2Te4) series, where the insertion of non-magnetic spacer layers yields modified magnetic properties [2,3]. In the main part of the talk, I will present more recent efforts to achieve 2D MnBi2Te4 layers using molecular beam epitaxy [4]. A particular focus will be on the realization of a single MnBi2Te4 monolayer, which shows robust 2D ferromagnetism below Tc = 14 K. As demonstrated by angle-resolved photoemission (ARPES), a monolayer MnBi2Te4 placed on Bi2Te3 induces a large magnetic gap in the topological surface state, promising realization of a robust quantum anomalous Hall state.

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5:00pm **MI-TuA-9 Rashba-Type Splitting of the Au(110) Surface State: A Combined Inverse and Direct Photoemission Study***, **Markus Donath**, K. Ritter,* University of Münster, Germany*; K. Miyamoto, T. Okuda,* Hiroshima University, Japan

The Shockley surface state located at Y on the (1×2)-reconstructed Au(110) surface is predicted to exhibit a Rashba-type spin splitting. Previous photoemission experiments searched for this splitting but it could not be resolved yet. In order to uncover a possible splitting, the unoccupied surface state on Au(110) is examined with spin- and angle-resolved inverse photoemission, whereas Na-covered Au(110) allows for investigation of the now occupied surface state by means of spin- and angle-resolved direct photoemission [1]. Our data show clear spin splittings in the order of 100 meV with a sign reversal at Y in the surface state's in-plane spin components which is characteristic for a Rashba-type behavior. Furthermore, we deduce an effective mass of $m^* = (0.27 \pm 0.02)m_e$ and a Rashba parameter of $\alpha_R = (0.46 \pm 0.04)$ eVÅ from direct photoemission measurements.

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5:20pm **MI-TuA-10 Spin-Polarized Resonant Tunneling - a New Tool for Sensing and Manipulating Magnetism on the Atomic Scale***, **Anika Schlenhoff**,* Department of Physics, University of Hamburg, Germany **INVITED**

Atomic-scale magnetism as found in ultrathin films with non-collinear spin textures or in moiré structures of 2D-hybrid materials raise expectations for potential spintronic applications, demanding for atomic-scale, spin-sensitive, but yet robust techniques for sensing and manipulation. Spin-polarized image-potential states (sp-IPS) are unoccupied electronic states in the vacuum gap between a probe tip and a magnetic sample. They exhibit the same local spin quantization axis as the surface, even when it rotates on the atomic scale [1]. In a spin-polarized scanning tunneling microscopy (SP-STM) setup, spin-polarized electrons can tunnel resonantly from the magnetic tip via the sp-IPS into the surface, resulting in a magnetic image contrast mediated by these states.

Our SP-STM experiments on non-collinear spin textures in ultra-thin films demonstrate that the spin-polarized resonant electron tunneling via sp-IPS allows for atomic-scale spin-sensitive imaging in real space at tip-sample distances of up to 8 nm, providing a loophole from the hitherto existing dilemma of losing spatial resolution when increasing the tip-sample distance in a scanning probe setup [2]. Technically applicable to a variety of material systems, our spin-polarized resonant tunneling studies on iron- and cobalt-intercalated graphene show that the IPS's sensitivity to the interlayer coupling of graphene to the metallic substrate and the resulting local IPS spin-polarization can be used for probing the graphene magnetism in the moiré unit cell [3].

When the electrons relax from the sp-IPS into the surface, a spin-transfer torque (STT) is exerted on the sample that can be exploited for thermally-assisted magnetization switching [4]. On ferromagnetic nano-islands, we observe IPS that are bound to the rim of the islands, causing a spatial modulation of the IPS electron spin-polarization above the uniformly magnetized nanoislands. As I will show, tunneling locally through the sp-IPS can be used to tune the spin-polarization of the resonant tunneling current and thus the STT for current-induced magnetization switching, using the sp-IPS as a spin-filter [5].

Utilizing the local spin-polarization of IPS via spin-polarized resonant tunneling, our approach qualifies for a spin-sensitive read-write technique with ultimate lateral resolution, potentially opening a pathway towards future technical applications.

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Plasma Science and Technology Division
Room 305 - Session PS1+TF-TuA

Plasma Processing for Advanced Emerging Memory Technologies, Advanced Packaging and Heterogeneous Integration

Moderators: Hisataka Hayashi, KIOXIA, Japan, **Samson Odunuga**, Intel Corporation

2:20pm **PS1+TF-TuA-1 Study of Residues Formation after Ge-Rich GST Etching Using Halogen Gases*, Benjamin Fontaine,*** STMicroelectronics, France*; C. Boixaderas,* Univ. Grenoble Alpes, CEA, Leti, France*; J. Dubois, P. Gouraud, A. Rival,* STMicroelectronics, France*; N. Posseme,* Univ. Grenoble Alpes, CEA, Leti, France

Non-volatile memories patterning is being more and more challenging with dimension reduction. Germanium-antimony-tellurium alloy (GST) has been well studied for phase-change random access memory (PCRAM) applications. Previous publications have proven the interest of using halogen plasmas to etch GST with etch rate range between 200 nm.min^{-1} and 700 nm.min^{-1} using HBr, CF_4 or Cl_2 chemistries. The etching results in halogen implantation in the first nanometers of the material with less modified surface and better roughness using the HBr chemistry. Despite these improvements, complementary analyses recently revealed a defectivity increase (residue formation) after etching and air exposure.

In this work, we propose to study the evolution of the surface state from the first hours of air exposure to several days after the etching using Ge-rich GST full-sheets. We compared the halogen chemistries showing residues formation in the first moments of air exposure after the etching step. Throughout a kinetic study, we showed the criticality of brief air exposures and found the optimal time required for the material protection.We observed a high level of defectivity after 24h of air exposure.

Residues are known for altering devices operation. XPS and EDS analyses revealed that important surface oxidation is present when residues appear. Complementary analyzes revealed that moisture environment has also a catalytic effect on the residue formation. Based on these results, a detailed mechanism responsible of residues formation will be presented. Using this mechanism, in-situ Post-Etching Treatments (PETs) will be proposed in order to prevent residues formation. We will implement the best PETs on real devices to verify their effectiveness.

2:40pm **PS1+TF-TuA-2 Magnetron Plasma Sputtered $Ge_2Sb_2Se_4Te$ as a Non-Volatile Optical Switch Material*, Steven Vitale,*** *P. Miller, P. Robinson, C. Roberts, V. Liberman,* MIT Lincoln Laboratory*; Q. Du, Y. Zhang, C. Popescu, M. Shalaginov, T. Gu,* Massachusetts Institute of Technology*; M. Kang, K. Richardson,* University of Central Florida*; C. Rios,* University of Maryland*; J. Hu,* Massachusetts Institute of Technology

Commercial technologies such as non-volatile memory, integrated photonic circuits, and compact optics are enabled by amorphous-to-crystalline transition of phase change materials (PCMs); for optical applications, the key feature of PCMs is the ability to change the optical properties (n, k) of the material by switching between a high-index crystalline phase and a low index amorphous phase. Here, we study the phase transition of an IR-transparent PCM, $Ge_2Sb_2Se_4Te$ (GSST), deposited using an AJA combinatorial magnetron plasma sputtering system. The film composition was tuned by varying the RF power to each of the Ge, Sb, Te, and $GeSe_2$ sputtering targets based on measurements from an in-situ EDX spectrometer.

Microheaters were fabricated in a fully-depleted silicon-on-insulator technology and coated with GSST. Microheater temperatures in excess of the melting point of GSST (900 K) were achieved. The small mass of the microheater allows for a quenching rate in excess of 10^7 K/s which is critical for amorphization as slower cooling causes recrystallization. The microheater chips were mounted in a Raman microscope and connected to pulsed electronics and the GSST structures was measured after amorphization or recrystallization heater pulses. The characteristic Raman peak of amorphous GSST occurs at 157 cm^{-1} and is consistent with Ge-4Se tetrahedral units. The characteristic Raman peak of crystalline GSST occurs at 120 cm^{-1} and is consistent with Ge-6Se octahedral units. The fundamental crystalline-to-amorphous transition appears to be reduction in Ge coordination from six to four, with the excess selenium atoms forming an amorphous Se-Se network. The amorphous-to-crystalline transition requires breaking the Se-Se network and increasing the Ge coordination from four to six. The measured activation energy for this transition is very close to the Se-Se bond energy and is thus consistent with the proposed mechanism. Enabled by the microsecond heater response we measured an ultrafast time-temperature-transformation diagram for GSST.

No irreversible chemical change (such as oxidation or decomposition) was observed up to 1000 crystallization-amorphization cycles. Lumerical simulations of a telecom-relevant silicon photonic switch show that the measured variation in octahedral/tetrahedral content allows for acceptable insertion loss variability but improved microheater temperature reproducibility will reduce variation in output port contrast.

3:00pm **PS1+TF-TuA-3 Phase-Change Memory Materials Processing Requirements*, Luxherta Buzi,*** IBM Research Division, T.J. Watson Research Center*; H. Cheng,* Macronix*; M. Hopstaken,* IBM Research Division, T.J. Watson Research Center*; L. Gignac,* IBM Research, T. J. Watson Research Center*; C. Tabachnick, J. Papalia, H. Miyazoe, S. Engelmann, R. Bruce,* IBM Research Division, T.J. Watson Research Center

Switching of Phase Change Memory (PCM) material between crystalline and amorphous phase with electrical pulses and optical properties make it an important candidate for storage class memory and neuromorphic computing [1-2]. These PCM materials (e.g., GeSbTe and its derivatives) can be damaged during plasma etch processing leading to poor performance and yield [3-4]. Surface oxidation of PCM materials can substantially alter switching properties therefore, in-situ encapsulation has been viewed as a favorable solution [5]. It is imperative that RIE and encapsulation mitigate damage or oxidation of PCM material during integration. This paper reviews the effects of etch chemistry, temperature, plasma reactor, and post RIE processing on material properties [3, 6]. In-situ encapsulation of GST and tuning of plasma parameters, caused controlled SiN film deposition with simultaneous selective etching of GST [6]. We have also demonstrated that using alternative chemistry for PECVD film encapsulation can improve GST switching properties and provide a good barrier for GST oxidation.

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3:20pm **PS1+TF-TuA-4 Exploration of Alternative Hard Mask Materials for the IBE Patterning of 50nm Pitch STT-MRAM High Density Orthogonal Pillar Array*, Romuald Blanc*,** *L. Souriau, W. Devulder, S. Couet, F. Lazzarino,* IMEC, Belgium

In order to approach the bit density of dynamic random access memory (DRAM), spin-transfer torque (STT) magnetic random access memory (MRAM) requires to be scaled down to pitch 50nm and below[1,2]. To fabricate 50nm pitch STT-MRAM high density pillars, ion beam etching (IBE) is used to pattern the magnetic-tunneling junction (MTJ). This etch technique relies mainly on physical ion sputtering which does not allow high selectivity to the hard mask[3], therefore a robust material is needed to avoid excessively thick hard mask and high pillar aspect ratio.

In this talk, we present the etch rate of multiple materials deposited in 300mm production tools etched with different with ion beam etching conditions. Then we demonstrate the patterning of a hybrid hard mask composed of high-density diamond-like carbon (DLC) to increase etch selectivity and TiN which will become the STT-RAM top electrode. Finally, the interest of this hybrid DLC/TiN hard mask is evaluated for the patterning of the MTJ stack with IBE.

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4:20pm **PS1+TF-TuA-7 Patterning Approaches for Integration of Complex Metal Alloys Towards Advanced Memory and Compute Applications*, Shreya Kundu*,** *F. Lazzarino,* IMEC, Belgium **INVITED**

Increasing need of data processing from core electronic devices is instrumental in driving the innovation of high-density memories and high-performance computing in the semiconductor industry. To sustain this growth in storage and computing domains, novel material systems are being investigated exhaustively due to their promising intrinsic properties. A key challenge here is their satisfactory patterning to enable assimilation into integrated chips.

Patterning studies of complex alloy systems generally aim at finding a suitable etch chemistry which promises good feature profiles with minimal physical and chemical damage. However, when integrated with diverse electrode materials (for e.g. SiN, TiN), it becomes imperative for the patterning investigation to include an additional criterion i.e., the etching of the novel alloy or the electrode should not have an adverse morphological or structural impact on one another, as it can lead to poor electrical performance. Patterning of two types of complex material systems – chalcogenide-based films (GeSbTe, SiGeAsTe/Se) and InGaZnO (IGZO) – displaying etching attributes on opposite ends of the spectrum are discussed here. Chalcogenides find widespread application in resistive, holographic non-volatile memory, and ovonic threshold switches due to their unique electronic and optical response signatures. Therefore, these materials are often integrated with optically conductive electrodes and heat sinks within an electrical circuit[1]. As chalcogenides produce highly volatile halogen-based by-products[2], prolonged exposure to similar etchants used in conventional electrode patterning schemes can cause severe undercuts leading to feature collapse. On the other hand, IGZO, a potential candidate for high performing thin film transistors[3], can be patterned using a hydrocarbon etchant and remains unimpacted by the chemistries used for etching electrode materials[4]. However, IGZO-based residues along electrode sidewalls are common post-patterning, thereby making the devices prone to current leakage.

In this talk, an overview of challenges encountered in patterning complex materials in varied integration schemes is presented followed by a systematic discussion on etch approaches to circumvent them. The repeatability and scalability of the etching schemes are also discussed.

Acknowledgments- to IMEC's Industrial Affiliation Program, IMEC's Active Memory and TIP integration team.

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5:00pm **PS1+TF-TuA-9 Plasma Etch Challenges and Processing Optimization in Spin Logic Device Fabrication*, Yann Canvel,*** *L. Souriau,* IMEC, Belgium

Presently, microprocessor chips rely on the networking of billions of tiny switches, commonly called transistors. These CMOS-based technologies run logic operations via the electron charge to enable data computing for the function of any digital object. In the development of next-generation logic devices, an alternative solution would be to leverage the electron's spin instead of the electron's charge. This specific electron manipulation paves the way towards the fabrication of spin logic devices which promises high performances and low power consumption.

In this communication, close attention will be dedicated to the unique patterning challenges of such architectures. It mainly consists of creating a magnetic interconnect system to propagate, in a controlled way, the information through the magnetic logic circuit. Ion Beam Etch (IBE) technique is used to shape the magnetic track. The critical point is to control the vertical etch of the Magnetic Tunnel Junction (MTJ) stack at nanometric scale. In this frame, a deep understanding of the plasma-surface interaction is required and will be presented here. As a result, some process optimization will be discussed to mitigate the ion-induced damages. Both soft landing and cyclic IBE approaches will be highlighted as proof of concept.

Raymenants, E. *et al.* Nanoscale domain wall devices with magnetic tunnel junction read and write. *Nat Electron***4**, 392–398 (2021).

Raymenants, E. *et al.* All-Electrical Control of Scaled Spin Logic Devices Based on Domain Wall Motion. *IEEE Trans. Electron Devices***68**, 2116–2122 (2021).

Raymenants, E. *et al.* Magnetic domain walls: from physics to devices. in *2021 IEEE International Electron Devices Meeting (IEDM)* 32.3.1-32.3.4 (IEEE, 2021).

5:20pm **PS1+TF-TuA-10 Effects of Bias Frequency on High Aspect Ratio Etching Using Voltage Waveform Tailoring*, Florian Krüger,*** University of Michigan*; H. Lee, S. Nam,* Mechatronics Research, Samsung Electronics Co., Ltd., Republic of Korea*; M. Kushner,* University of Michigan

The continuing reduction of feature sizes and increasingly high aspect ratios (HAR) in plasma etching pose major challenges to high volume manufacturing of nanoscale semiconductor devices. Capacitively coupled plasmas (CCPs) are an important tool for HAR etch processes. In these systems, the DC self-bias is used as a measure of mean ion energies incident onto the wafer. DC bias is coupled to the asymmetry of the system which can be a function of geometry, material differences, magnetic configurations and the use of non-sinusoidal voltage waveform tailoring (VWT) through the electrical asymmetry effect.

We computationally investigated the consequences of bias frequency on ion energy distributions (IEDs) and SiO_2 etch properties when varying the electrical asymmetry of the bias waveform.The electrical asymmetry is controlled with the phase shift of the even harmonics ϕ of a multifrequency waveform.The system is a CCP with high frequency source power and low frequency bias power.The plasma was sustained in fluorocarbon gas mixtures at 40 mTorr. The bias waveform consisted of 5 harmonics with a base frequency of 1 to 10 MHz. The gas phase simulations were performed using the Hybrid Plasma Equipment Model (HPEM).Using reactive fluxes to the wafer from the HPEM, etching of a HAR via in SiO_2 was simulated using the Monte Carlo Feature Profile Model.The resulting features were evaluated based on etch rate, etch depth and distortion.

We found that at sufficiently high bias frequencies where ions are unable to react to time-varying fields in the sheath, IEDs are dominantly affected by time-averaged sheath electric fields. Mean ion energy is correlated to the DC self-bias, which in turn is correlated to ϕ**.** In this regime maximumion energies occur when $\phi=0$, and electrical asymmetry as well as DC self-bias magnitude are maximum. The resulting etch features have most desirable qualities when ion energies are high at low phase angle.

This trend does not apply and, in fact, reverses for low bias frequencies where ions are able to dynamically react to transient electric fields. This leads to temporal variations in ion energies and fluxes which result in higher ion energies at higher phase angles and lower electrical asymmetry. The trend of reversal in ion energies with phase angle also translates to the etch feature having better overall quality at high phase angle. We conclude that when using VWT techniques for process control in etch systems, there are two frequency regimes (dynamic-ions and stationary-ions) having different control mechanisms.

Work supported by Samsung Electronics and the National Science Foundation.

5:40pm **PS1+TF-TuA-11 Wafer Bevel Deposition by Localized SiO_2 and Si_3N_4 PECVD and Application to 3D Integration***, **Francois Boulard**, F. Fournel, V. Lapras, L. Brunet, D. Truffier-Boutry,* CEA-University Grenoble Alps, France*; P. Ruault,* Lam Research, France*; M. Keovisai,* Lam Research*; C. Porzier, V. Gros, N. Posseme,* CEA-University Grenoble Alps, France

As 3D integration schemes move forward new process challenges arise. One of them is to manage contamination issues of multiples stacked wafers. Particularly, wafers edge and bevel are known to be the source of delamination or defects, as metals or particles contaminations[1-3]. This is even more critical after bonding when back-end of line wafers are reprocessed on front-end tools[4]. In this paper, we present a strategy consisting in encapsulating the bevel area in a single process step. SiO_2 and Si_3N_4 are deposited by PECVD at 350°C on blanket 300mm Si and CMOS + 4 BEOL levels wafers. We study the influence of pressure, RF power, and single or dual frequency plasma excitation on deposition rate, refractive indexes, and films stoichiometries by XPS. No deposition occurs on most of the top surface since the gap between the wafer front side and the top grounded electrode remains below 1 mm. On the wafer edge and bevel, where plasma and deposition take place, films wet etch rates confirm oxide and nitride excellent qualities. The radial deposition profiles is characterized by ellipsometry and scanning electron microscopy cross section. The integration of bevel deposition on CMOS+M4 products is studied. We demonstrate the compatibility of the approach with top tier bonding and the effectiveness of the encapsulation to control BEOL metal contamination.

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6:00pm **PS1+TF-TuA-12 Plasma Etching of Copper for the Microfabrication of High-Density Interconnects in Advanced Packaging***, **Juliano Borges**, M. Darnon, Y. Beilliard, D. Drouin,* Université de Sherbrooke, Canada

Low-cost and high-density redistribution layers (RDL) in integrated circuits packaging are essential to support further development in the fields of high-performance computing and internet of things. Indeed, both require low-cost electronic systems capable of delivering higher bandwidths, improved operation speeds, and enhanced power performance, which can be done by in-package multi-chiplets interconnection.

Organic or silicon interposers have been developed to allow the connection of dies in 2D configurations. Even if silicon-based interposers offer the best interconnects density, they cannot be used in high-frequency applications due to the high resistive losses induced by silicon and their cost is prohibitive for consumer electronics applications. High-density RDL fabrication on organic interposers is therefore required for high-frequency operation and low-cost manufacturing. However, conventional organic interposer fabrication methods by semi-additive processes are not compatible with high-density RDL (<2 µm pitch) because of isotropic wet etching of the seed layer. On the other hand, damascene processes cannot be performed on organic substrates because of substrate warpage. We propose to revisit copper etching processes for high-density RDL fabrication on organic substrates.

Chlorine-based plasmas have been explored as an alternative for etching copper, generally employing cyclic approaches. $CuCl_2$ species are formed upon exposure to Cl radicals and can be transformed into volatile Cu_3Cl_3 when exposed to hydrogen [1]. We developed a one-step $Ar/Cl_2/H_2$-based plasma in an inductively coupled plasma (ICP) chamber with a cathode temperature of 200°C. Using this process, we demonstrated the anisotropic plasma etching of copper with an etch rate of 500 nm/min. A specific seasoning and cleaning process was also set up to provide reproducible etching conditions with no significant chamber contamination after cleaning. By optimizing the etch process, we were able to fabricate high-density copper-based RDL with a pitch of 2 µm. Preliminary tests validated the compatibility of the process with organic substrates.

These results demonstrate the capability of plasma etching processes to etch copper for the fabrication of high-density RDL on an organic substrate for advanced packaging applications.

[1]N. S. Kulkarni and R. T. DeHoff, "Application of Volatility Diagrams for Low Temperature, Dry Etching, and Planarization of Copper," J. Electrochem. Soc., vol. 149, no. 11, p. G620, Oct. 2002, doi: 10.1149/1.1513986.

Plasma Science and Technology Division
Room 315 - Session PS2+AS+SS-TuA
Plasma-Surface Interactions

Moderators: Pingshan Luan, TEL Technology Center America, **Kenji Maeda**, Hitachi High Technologies America Inc.

2:20pm **PS2+AS+SS-TuA-1 Selective Mask Deposition Using $SiCl_4$ Plasma for a Highly Selective Etching Process***, **Miyako Matsui**,* Hitachi Ltd., Japan*; K. Kuwahara,* Hitachi High-Tech Corp., Japan **INVITED**

The local cell size of logic devices has been continuously shrinking at a scaling rate of about 0.48 per 2 years. Extreme ultraviolet (EUV) lithography is a key technology for pitch scaling, though the pitch scaling rate has been slowing down since 2010. To boost the scaling, design technology co-optimization (DTCO) has been developed by using various kinds of self-aligned processes. However, process challenges exist for both technologies. Etching processes using thin EUV resists require extremely high selectivity and precise control of critical dimensions. Selective etchings for DTCO require high selectivity between layers having a similar material composition. In both cases, selective deposition for forming protective layers only on unetched materials can solve these process challenges and achieve extremely highly selective etchings.

In this study, we investigated a selective deposition process for forming protective layers on top of masks generated by a microwave-ECR etching system. A deposition layer was formed only on SiO_2 masks without forming an unnecessary deposition layer on Si surfaces of etching area, such as bottoms of the patterns and isolated etching area. This process effectively achieves extremely highly selective etchings by selectively forming the protective layers prior to the etching procedure in the same chamber.

We suggested a process for selectively forming protective layers on a SiO_2 without forming on a Si etching area by using a $SiCl_4/H_2/Cl_2$ plasma. Top surfaces of the materials needed to be cleaned before forming the protective layer. Selectivity is thought to be provided by the difference in $SiCl_x$ desorption processes. On the Si surface, adsorbed $SiCl_x$ easily desorbed again by reacting with Cl generated from the plasma. On the other hand, adsorbed $SiCl_x$ on SiO_2 was thought to be more difficult to desorb by reacting with Cl due to Si-O having larger binding energy than Si-Si. After the deposition layer was selectively formed on the SiO_2 mask, the layer was oxidized using an O_2 plasma treatment to improve the etching resistance during the Si-etching. The O_2 plasma treatment time was controlled not to prevent the Si substrate from being etched during the Si-etching. We found the optimum O/Si concentration of oxidized protective layer was about 0.4 from X-ray photoelectron spectra (XPS) analysis.

We also demonstrated the selective deposition to etch a line-and-space pattern with a SiO_2 mask. In this process, selective deposition, oxidation, and Si etching were cyclically carried out. The extremely highly selective etching was achieved using the selective deposition without forming an unnecessary deposition on an isolated Si area.

3:00pm **PS2+AS+SS-TuA-3 On the Self-bias Voltages at Sintered Yttrium Oxyfluoride (Y-O-F) and Y_2O_3 During Plasma Irradiation and Their Etching Rates due to Ion Bombardment***, **Tetsuya Goto,** Y. Shiba,* Tohoku University, Japan*; A. Teramoto,* Hiroshima University, Japan*; Y. Kishi,* Nippon Yttrium Co., Ltd, Japan*; S. Sugawa,* Tohoku University, Japan

Yttrium oxyfluoride (Y-O-F) has been received much attention as the bulk and/or coating materials for functional components used in the plasma process chamber in semiconductor manufacturing, because chemical component stability of Y-O-F against various corrosive plasmas is better than that of widely used Y_2O_3 [1-3]. In addition to the chemical component stability, etching rate of these materials is also an important issue when particle problem and lifetime of the components are considered in industry. Previous report has shown that the etching rate of Y-O-F and Y_2O_3 due to plasma irradiation is almost the same level [2]. On the other hand, we reported that, the etching rates of the sintered Y-O-F due to the Ar ion beam irradiation (without plasma) was clearly smaller than that of Y_2O_3 [3]. We speculated that such tendency was caused by higher atomic number density of Y-O-F than that of Y_2O_3. Thus, the etching behavior of Y-O-F and Y_2O_3 was different between the cases of the ion beam irradiation and the plasma irradiation.

In this report, to understand the observed difference in more detail, we measured self-bias voltage V_{dc} of surfaces of Y-O-F and Y_2O_3 samples set on Si wafer in 13.56-MHz excited capacitive coupling Ar plasma. Here, V_{dc}, which is approximately an acceleration voltage of ions, is a good parameter to estimate ion bombardment energy at the sample surface. It was found that $|V_{dc}|$ of Y_2O_3 was smaller than that of Y-O-F, suggesting that surface voltage condition was different under the normal setup of the samples for the plasma irradiation test. In this setup, etching rates of Y-O-F and Y_2O_3 due to Ar plasma irradiation were found to be almost the same.

Next, to equalize the surface voltages of Y_2O_3 and Y-O-F during the plasma irradiation as far as possible, we connected the sample surface and the Si wafer surface using electrically-conductive carbon tape. In this case, it was found that the etching rate of Y-O-F was smaller than that of Y_2O_3, showing the same behavior to the Ar ion beam etching experiment.

The results suggested that the intrinsic etching resistance of Y-O-F due to the ion bombardment is better than that of Y_2O_3. Also, the results showed the importance of how the sample was set in the plasma irradiation test to accurately estimate plasma resistance. Furthermore, it is considered that, in the actual plasma equipment, plasma resistance depends strongly on how the protect material was set or coated.

1. Y. Shiba et al, J. Vac. Sci. Technol. A, 35 (2017) 021405.

2. H. Ashizawa and K. Yoshida, Int J Appl Ceram Technol. (2021) 1.

3. T. Goto et al., J. Vac. Sci. Technol. A, 38 (2020) 043003.

4:20pm **PS2+AS+SS-TuA-7 In-Plasma Photo-Assisted Etching of Si with Chlorine Aided by an External Vacuum Ultraviolet Source***, L. Du, D. Economou,* ***Vincent M Donnelly,*** University of Houston

Photo-assisted etching (PAE) of *p*-type Si(100) was found to occur in a chlorine-containing, Faraday-shielded, inductively coupled plasma (ICP) with no substrate bias, attributed mainly to the vacuum ultraviolet (VUV) light generated by the plasma. Other causes for the very high etching rates can be ruled out, including ion bombardment-assisted etching and chemical etching by Cl atoms. Masked samples produced slow etching (111) facets and smooth surfaces. To provide additional evidence for the VUV-PAE mechanism, the substrate in a main Cl_2/Ar ICP was subjected to extra VUV light (mainly 104 and 106 nm Ar emission) that was generated in an independently controlled, auxiliary Ar/He ICP in tandem with the main ICP. The ICPs were separated by a tungsten mesh and a bundle of high-aspect-ratio quartz tubes in a honeycomb configuration. There was no measurable perturbation of the main plasma by the auxiliary plasma. The etching rate was found to be enhanced by 11 to 51% with the additional VUV light provided by the auxiliary ICP. Absolute measurements of the auxiliary ICP photon flux at the surface were obtained in-situ by recording photoemission yields from a Au-coated sample in place of the Si substrate. Incredibly large etching yields of 90 to 240 Si atoms-per-photon were obtained. It is argued that etching is not a result of electron-hole pair formation, but is instead ascribed to a photo-catalytic chain reaction. No etching occurs with just $Cl_{2(g)}$ and the auxiliary VUV source, hence Cl atoms produced by the main ICP are required to produce the more highly chlorinated surface required for propagation of the chain reaction.

4:40pm **PS2+AS+SS-TuA-8 Etching of Silicon Dioxide (SiO_2) Based on Remote Plasma-Based Functionalization and Electron Beam-Activation***, **Yudong Li,** K. Lin,* University of Maryland, College Park*; C. Preischl, C. Hermanns, D. Rhinow, H. Solowan, M. Budach, H. Marbach, K. Edinger,* Carl Zeiss SMT, Germany*; G. Oehrlein,* University of Maryland, College Park

Electron-beam stimulated activation of SiO_2 surfaces functionalized by remote plasma is demonstrated as a promising novel approach to achieve atomic scale etching. Compared to conventional plasma-based dry etching utilizing ion bombardment, electron-beam induced etching (EBIE) avoids ion-induced damage effects such as atomic displacement and atomic mixing. One issue with EBIE is the limited number of chemical precursors that is available to functionalize substrate surfaces without spontaneous etching.

In this work, we demonstrate a new approach that combines surface functionalization by a remote plasma source and energy deposition using an electron beam source to enable EBIE. A prototypical case is SiO_2 etching using $Ar/CF_4/O_2$remote plasma generated precursors and electron-beam initiated removal of the chemically reacted surface layer by low-energy electron bombardment. We evaluated the parametric dependence of SiO_2etching on remote plasma source and electron flood gun operating parameters, including radiofrequency (RF) source power, CF_4/O_2 flow composition, electron energy and emission current, respectively. Two prototypical processing cases were examined: one simultaneous and two sequential remote plasma treatment and electron beam irradiation. Material selective atomic scale etching of Si_3N_4 over SiO_2 and poly-Si over SiO_2 were demonstrated. Surface chemcial modification and etching were followed by in-situ ellipsometry measurements. Surface chemical changes were also characterized by x-ray photoelectron spectroscopy and revealed mechanistic insights for these processes.

We gratefully acknowledge the financial support of this work by ZEISS SMT GmbH.

5:00pm **PS2+AS+SS-TuA-9 Investigation of Plasma-Surface Interactions During Plasma Enhanced Atomic Layer Deposition (PE-ALD) of Silicon Nitride Using *in Situ* Surface Chemistry Measurements***, **Samuel Johnson,*** University of Texas at Austin*; J. Zhao, T. Iwao, J. Carroll, C. Schlechte, P. Ventzek,* Tokyo Electron America*; J. Ekerdt,* University of Texas at Austin

A low temperature process for silicon dielectric thin film deposition is necessary for a wide range of semiconductor process applications, including as spacers in FinFET and self-aligned multiple patterning. Using plasma enhanced atomic layer deposition (PE-ALD) with radio frequency (RF) power to deposit silicon nitride films is very promising as it lowers the deposition temperature compared to thermal atomic layer deposition; however, direct plasma enhanced processes face a difficulty of guaranteeing the conformality of film thickness and film properties on high aspect ratio, 3-dimensional device structures. Ionized plasma species have a high degree of directionality, resulting in differences between top facing and sidewall surface coverage and properties. Ion beam incoherency, which can be tuned by varying the frequency and pressure, may be used to achieve more property conformity.

To explore the PE-ALD of silicon nitride, we built a radio frequency capacitively-coupled plasma (CCP) PE-ALD chamber.Our PE-ALD process involves one half cycle of dichlorosilane (DCS) gas for silicon layer adsorption, and another half cycle of an ammonia/argon plasma for nitridation. We used three different RF frequencies in deposition experiments on planar surfaces and a 3-dimensional trench-patterned surface in a silicon substrate. We have investigated the bulk film and surface chemistry using *in situ* X-ray photoelectron spectroscopy (XPS) and *in situ* Fourier-transform infrared spectroscopy (FTIR). With increasing frequency, the overall $N-H_x$ bonding decreased (a higher percentage of nitrogen bonds were unsaturated), and the remaining $N-H_x$ bonds became rich in $N-H_2$ bonds compared to N-H bonds. Further details will be discussed on the correlations between the plasma characteristics (ion energy and angle, neutral flux, etc.), the *in situ* surface chemistry measurements, and the film properties.

5:20pm **PS2+AS+SS-TuA-10 Differences in Sidewall Chemistry for SiO_2 and Si_3N_4 after Ar/HFC or Ar/FC Plasma Processing Using High Aspect Ratio Structures***, **Sang-Jin Chung,*** University of Maryland, College Park*; P. Luan, A. Metz, M. Park,* TEL Technology Center, America, LLC, USA*; G. Oehrlein,* University of Maryland, College Park

State-of-the-art 3-dimensional memory devices utilize high-aspect-ratio (HAR) heterogeneous structures where 2 or more materials are etched simultaneously during the fabrication process. Controlling the sidewall chemistry of stacked materials etched using the same fluorocarbon (FC) or hydrofluorocarbon (HFC) process is one of the key factors for yielding excellent etch profiles. Here, we use a horizontal trench gap structure [1,2] to simulate the interaction of neutral radicals produced by FC and HFC plasma with SiO_2 and Si_3N_4 sidewalls in HAR structures for aspect ratios (AR) of up to 90. Oxide and nitride trench structures were simultaneously treated with Ar/FC or Ar/HFC plasma without RF bias and changes in film thickness were probed by ellipsometry as a function of AR. We find a variety of responses of the trench sidewalls for the remote plasma conditions, including both polymer deposition and spontaneous etching. These responses are dependent on the type of FC and HFC gases, the surfaces being exposed, and the position relative to the trench entrance. For HFC chemistry, oxide shows relatively little etching near the trench entrance followed by the presence of a very thin FC layer (<1 nm) for increasing AR. For the same conditions Si_3N_4 shows significantly more etching both near the entrance and for high AR deep in the structure. For FC plasma the behavior is different and polymer deposition is primarily seen for the high-AR trench structures. These observed behaviors are further correlated to the scalloping phenomenon commonly seen in layered ONO HAR structures. We will also discuss the surface responses with in-situ characterizations, including optical emission spectroscopy (OES), and FC deposition rate measurements seen for directly exposed SiO_2 or Si_3N_4 surfaces.

[1] Zheng, L., Ling, L., Hua, X., Oehrlein, G. S. & Hudson, E. A. Studies of film deposition in fluorocarbon plasmas employing a small gap structure. *J. Vac. Sci. Technol. A Vacuum, Surfaces, Film.* 23, 634–642 (2005).

[2] Knoll, A. J., Pranda, A., Lee, H. & Oehrlein, G. S. Substrate temperature effect on migration behavior of fluorocarbon film precursors in high-aspect ratio structures. *J. Vac. Sci. Technol. B.* 37, 031802 (2019).

5:40pm **PS2+AS+SS-TuA-11 Significance of Plasma-Surface Interactions in the Etch Behavior of Low-k Materials***, **Adam Pranda**, S. Grzeskowiak, Y. Yoshida, E. Liu, Y. Han, P. Biolsi,* TEL Technology Center, America, LLC*; K. Kobayashi, N. Ikezawa,* Tokyo Electron Miyagi Ltd., Japan

Low-k materials are an integral component in the advancement of semiconductor device performance by reducing parasitic capacitance and enabling faster device switching for a given thickness compared to traditional dielectric materials such as SiO_2. With the advances in logic scaling, low-k materials are increasingly more prominent in the structures of advanced devices. For example, low-k materials are being targeted as the inner spacer ingate-all-around (GAA) nanosheet field effect transistors. Consequently, the integration of low-k materials requires that the etch behavior of these materials be well understood so that the device structures can be reliably and reproducibly fabricated. In this study, we used a high-density plasma reactor with benchmark CF_4- and NF_3-based process chemistries to etch low-k materials including SiCN, SiOCN, and SiBCN along with reference materials including Si, SiO_2, and SiN. We utilized a characterization suite consisting of optical emission spectroscopy (OES), mass spectroscopy (MS), spectroscopic ellipsometry (SE), x-ray photoelectron spectroscopy (XPS), and attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) to understand the relationships between the plasma conditions (OES, MS), the evolution of the surface chemistry of the materials (XPS, ATR-FTIR), and the resulting etch behavior (SE). The etch behavior of low-k materials under a given etch process is vital for establishing the etch selectivities in multilayer structures that are required to yield complex device geometries. For example, we found a correlation in the relative magnitude of OES trend for the CN emission at 387nm to the low-k material etch rate, which suggests that preferential sputtering of the nitrogen and possibly carbon from the sample is one of the main pathways for the etching of nitrogen-containing low-k materials. Identifying the underlying mechanisms for the etch behaviors of low-k materials will provide key guidance into the development of etch processes that integrate these materials in current and future device structures.

6:00pm **PS2+AS+SS-TuA-12 Low Temperature Superpermeability in Metal Foils Exposed to Hydrogen Plasma***, **Chao Li**, A. Job,* Colorado School of Mines*; M. Shimada, T. Fuerst,* Idaho National Laboratory*; D. Way, C. Wolden,* Colorado School of Mines

The hydrogen isotopes tritium (T) and deuterium (D) are leading fuels for use in future fusion reactors. In these reactors they combine to form He and an energetic neutron in a high density, magnetically confined plasma. Metal foil pumps are a technology to extract the unreacted isotopes from the He ash in the plasma exhaust and return them to the plasma in a process known as direct internal recycling. Hydrogen separation membranes typically work through a dissociative adsorption - atomic diffusion - recombinative desorption mechanism that relies on a hydrogen partial pressure gradient. Unlike molecular hydrogen, energetic H atoms and ions can bypass the dissociation/absorption step and directly enter the metal. This leads to hydrogen fluxes that can be orders of magnitude greater than expected from Sievert's law, a condition described as superpermeability. In this study, we investigate the superpermeability of various metal foils (PdAg, V and α-Fe) exposed to inductively coupled H_2 plasma operating at low temperature (50-200 ^oC) and the results are compared to a fundamental model accounting for individual steps in hydrogen permeation. Systematic variation of foil temperature and plasma parameters were used to illuminate the key rate limiting steps in the mechanism. Interfacial treatments including oxidation, plasma cleaning, and the deposition of nanoscale interfacial layers were used to modify surfaces to improve the hydrogen permeation of metal foils. Auger and AFM characterization were used to study the surface elemental composition and metal surface roughness, respectively. Both H_2 and D_2 plasmas were employed to better understand isotope effects. V foils with symmetric Pd deposition on both sides showed comparable permeation performance to PdAg foil with hydrogen flux exceeding 10^{20} m^{-2} s^{-1}. On the other hand, plain α-Fe foils showed very stable, but lower (10^{19} m^{-2} s^{-1}) hydrogen flux performance in repeated tests. Our findings suggest that V and α-Fe with appropriate surface modification are promising candidates for use as metal foil pumps for direct internal recycling of DT fuels in future fusion reactors.

Surface Science Division
Room 319 - Session SS+2D+AS-TuA

Structure, Adsorption and Reaction at 2D Material Surfaces

Moderators: Florencia C. Calaza, Instituto de Desarrollo Tecnológico para la Industria Química, Argentina, **Arthur Utz**, Tufts University

2:20pm **SS+2D+AS-TuA-1 Chemically Identifying Single Adatoms with Single-Bond Sensitivity During Oxidation Reactions of Borophene***, L. Li, N. Jiang, **Sayantan Mahapatra**,* University of Illinois - Chicago

The chemical interrogation of individual atomic adsorbates on a surface significantly contributes to understanding the atomic-scale processes behind on-surface reactions. However, it remains highly challenging for current imaging or spectroscopic methods to achieve such a high chemical spatial resolution. Here we show that single oxygen adatoms on a boron monolayer (i.e., borophene) can be identified and mapped via ultrahigh vacuum tip-enhanced Raman spectroscopy (UHV-TERS) with ~4.8 Å spatial resolution and single bond (B–O) sensitivity. With this capability, we realize the atomically defined, chemically homogeneous, and thermally reversible oxidation of borophene via atomic oxygen in UHV. Furthermore, we reveal the propensity of borophene towards molecular oxygen activation at room temperature and phase-dependent chemical properties. In addition to offering atomic-level insights into the oxidation of borophene, this work demonstrates UHV-TERS as a powerful tool to probe the local chemistry of surface adsorbates in the atomic regime with widespread utilities in heterogeneous catalysis, on-surface molecular engineering, and low-dimensional materials.

2:40pm **SS+2D+AS-TuA-2 Tailoring the Interfacial Properties of 2D Transition Metal Silicates on Metal Supports***, N. Doudin, K. Saritas,* Yale University*; J. Boscoboinik, G. Li,* Brookhaven National Laboratory*; S. Ismail-Beigi, **Eric Altman**,* Yale University

Two-dimensional (2D) transition metal (TM) silicates have the potential to add magnetic, piezoelectric, and multiferroic functionalities to the toolkit of 2D layers used to develop new technologies. To date, these 2D TM silicates have been chemically bound to the growth substrate through oxygen atoms; the ability to weaken the interaction with the substrate to isolate the materials as single vdW layers is crucial for realizing their potential. Hydration or hydrogenation of the 2D TM silicate presents an ideal modification methodology to pacify the bonds to the substrate and create tailored interface properties and functionalities. Towards this end, here we report the interaction of Au- and Pd-supported 2D TM silicates with H_2O, H_2, and O_2. We employed a range of characterization tools to assess the materials before and after treatment with the probe molecules. Ambient pressure x-ray photoelectron spectroscopy (AP-XPS), ambient pressure infrared reflection absorption spectroscopy (AP-IRRAS), low energy electron diffraction (LEED), and scanning tunneling microscopy (STM) in conjunction with first principles theory were utilized to assess surface morphology, interface characteristics, surface chemistry, and chemistry in in the confined spaces between the 2D TM silicate and metal support. The interaction of probe molecules with TM silicates on Pd(111) and Au(111) was studied over wide pressure (10^{-6}–1 mbar) and temperature (300–600 K) ranges. The data show that the dissociative adsorption of H_2 takes place to form OH bonds on the oxide surfaces under UHV conditions. When the pressure is increased to several mbar, the metal silicate surfaces are saturated with H atoms at 300 K. Exposure to H_2 at higher surface temperatures (≥ 600 K) reduces the TM silicate. Also, water dissociates readily on the metal silicate surfaces at 300 K. With an increase in H_2O pressure, a greater degree of surface hydroxylation was observed for all samples. At 1 mbar H_2O, molecular and dissociated water coexist (hydrogen bond OH/H_2O). In temperature-dependent studies, desorption of weakly bound water and surface dehydroxylation were observed with increasing temperature. Via AP-XPS combined with IRAS we study in detail the interaction of oxygen with the oxide surfaces, which shows that H_2-induced reduction can be reversed and the original structure restored. Our studies provide an effective avenue to achieve hydrated metal silicate layers and shed light on how to tune the chemical reactions of these overlayers by choosing suitable substrates.

3:00pm **SS+2D+AS-TuA-3 Metal Oxide and Metal Dichalcogenide 2D Nanocrystals: Structure, Adsorption and Catalytic Properties***, **Jeppe V. Lauritsen**,* Aarhus University, Denmark **INVITED**

Nanocrystals of two-dimensional materials may exhibit fascinating optical, electronic or chemical properties. In heterogeneous catalysis, the edge sites of some planar metal oxide and metal sulfide nanocrystals have been demonstrated be far more active than the majority sites exposed on basal planes. These observations have motivated us to obtain a better understanding of the edge site structure of 2D nanocrystals and try to establish the fundamental connection to their behavior in heterogeneous catalysis and electrocatalysis. I will discuss two examples showing how we investigated the structure and adsorption properties at the atomic scale by using scanning tunneling microscopy (STM) and photoemission spectroscopy techniques (XPS) on well-defined planar 2D nanocrystals supported on model substrates:

i. We used to atom-resolved STM images investigate edge reactivity of monolayer $CoOOH_x$ particles, widely considered as the active phase of cobalt-based catalysts in alkaline electrochemical water splitting. Water exposure experiments combined with atom-resolved STM imaging directly show an increased capacity to dissociate water on the edge sites, which is further substantiated by theoretical modelling [1]. Moreover, addition of Fe has strong promotional effect on the oxygen evolution. We have compared how the $CoOOH_x$ nanocrystals and chemical composition develops after the sample has been used as the working model electrode directly in a homebuilt *in situ* electrochemical cell attached to the STM chamber [2]. Our activity measurements confirm the expected increased oxygen evolution (OER) activity for Co-oxides mixed with Fe, which however depends in a highly non-linear way on the actual Fe content. Based on this information we found a model where the main effect of Fe doping in Co oxide is that of a structural edge stabilizer [3].

ii. MoS_2 nanocrystals are active catalysts in heteroatom extrusion from hydrocarbons (O, N, S) in oil and bio-oil processing (hydrotreating). Atom-resolved STM studies of MoS_2 nanocrystals as a supported model catalysts was used in combination with DFT analysis of molecule adsorption on MoS_2 edge to evidence an interesting new mechanism where adsorption of heteroatom-bearing hydrocarbons on a vacancy pushes neighboring S atoms aside. Thereby the adsorption event itself creates better catalytic active sites capable of adsorbing large hydrocarbons, explained the unusually wide selectivity of MoS_2 towards these reactions [4].

[1] J. Fester, et al., Nat. Comm **8**, 14169 (2017).

[2] Z. Sun, et al., Rev. Sci. Inst. **92**, 094101 (2021).

[3] Z. Sun, et al., ACS Nano **15**, 18226 (2021).

[4] N. Salazar, et al., Nat. Comm **11**, 4369 (2020).

4:20pm **SS+2D+AS-TuA-7 Intercalated $Cu_{2-x}O$ Thin Film Confined Underneath Hexagonal Boron Nitride***, **J. Trey Diulus**, Z. Novotny, N. Dongfang, N. Comini, J. Beckord, Y. Al-Hamdani,* University of Zurich, Switzerland*; M. Muntwiler,* Paul Scherrer Institute, Switzerland*; M. Hengsberger, M. Iannuzzi, J. Osterwalder,* University of Zurich, Switzerland

Confined catalysis has been achieved in zero and one dimensions using zeolites, metal-organic frameworks, and carbon nanotubes for optimized catalytic performance. Confinement can also be achieved in two dimensions by intercalation of reactants between solid layers. 2D materials grown on metal surfaces have become widely used model systems to study 2D-confined catalysis. Yet, numerous transition metals have been found to be more active in their oxidized form. Unfortunately, the growth of h-BN *via* chemical vapor deposition (CVD) has proven to be more difficult on metal oxides than on metals. Instead, a metal substrate underneath an h-BN monolayer can be oxidized *via* O_2 intercalation. Due to weak interactions between h-BN and Cu(111), the Cu(111) substrate is a prime candidate for intercalated oxidation, forming a thin oxide film (~3 Å) while the h-BN remains intact. Growth of h–BN on Cu(111) was achieved through CVD by borazine exposure in ultra-high vacuum at the In Situ Spectroscopy beamline at the Swiss Light Source (SLS). The surface structure, chemical composition, and uniformity of the as-grown h-BN/Cu(111) heterostructure were determined with low-energy electron diffraction, Auger electron spectroscopy, and X–ray photoelectron spectroscopy (XPS). Oxidation of the Cu(111) under h-BN *via* O_2 intercalation was executed by exposure to near-ambient partial pressures of O_2 (0.001 to 1 mbar) at temperatures ranging from 25 to 200 °C. Ambient pressure XPS and X-ray absorption spectroscopy were utilized at each temperature and pressure to determine the oxidation state of Cu and develop a recipe for preparing an ordered h–BN/$Cu_{2-x}O$/Cu(111) heterostructure. Further characterization of an ordered h–BN/$Cu_{2-x}O$/Cu(111) was obtained at the PEARL beamline at the SLS. Scanning tunneling microscopy (STM) provided atomic-resolution imaging of the sample held at 78 K, displaying a Cu_2O-like structure. STM further shows the oxidation of the Cu(111) substrate occurs *via* O intercalation at the h-BN grain boundaries. Density functional theory calculations, X-ray photoelectron diffraction experiments, and multiple-scattering simulations using the Electron Diffraction in Atomic Clusters code, provided further structural information, suggesting O atoms first adsorb to HCP-Cu sites on Cu(111), followed by the formation of a Cu_2O-like trilayer in between the substrate and h–BN. Ultimately, we fully characterize the structure and oxidation mechanism of a well-defined nano–reactor system that is ideally suited to study reactions in confined space. Furthermore, we propose this preparation method can be applied to more systems comprising of a 2D monolayer on a metal substrate.

4:40pm **SS+2D+AS-TuA-8 Imaging Surface Defects on MoS_2***, **Blake Birmingham**,* Baylor University

MoS_2 is an exciting hydrogen evolution reaction (HER) catalyst that exhibits promising activity in acidic media. However, the role of density and reactivity of defect sites to the HER performance of MoS_2 is currently unclear. Up to now, correlation of localized HER activity to atomic scale defects have been inferred via ex-situ measurements, where the macroscopic electrode activity is determined via bulk electrochemical techniques and correlated with the number of active sites that are measured separately via nanoscale surface imaging such as Scanning Tunneling Microscopy (STM) or Transmission Electron Microscopy.

In the presented experiment, the structural and chemical properties of bulk mineral MoS_2 catalyst during HER were monitored in-situ by electrochemical scanning tunneling microscopy (EC-STM). The nanoscale structure of the MoS_2 is correlated with its electrochemical activity in 0.5 M H_2SO_4(aq) electrolyte. Defects on the MoS_2 basal plane were atomically resolved before and after several rounds of cyclic voltammetry (CV) measuring the HER current vs applied potential against a carbon reference. Atomically resolved imaging of the same nanoscale area before and after HER does not show an increase in atomic defect site density after prolonged HER probed by many rounds of CVs. This indicates that new sulfur vacancies are either not produced during HER on MoS_2 basal plane or are produced and immediately occupied by hydrogen atoms. The surface was imaged near the HER onset potential, the evolution reaction was directly imaged as strong local tunneling instability. The tunneling destabilization effect is strongest near the nanoscale defect sites potentially due to local hydrogen gas bubbling.

5:00pm **SS+2D+AS-TuA-9 Modifying 2D Transition Metal Dichalcogenides (TMDs) by Incorporating Excess Transition Metals***, **Matthias Batzill**,* University of South Florida **INVITED**

Crystal modifications in 2D materials can introduce new functionalities in these materials. Here we discuss compositional and structural crystal modifications in some transition metal dichalcogenides (TMDs). Specifically, we show that excess metals can be incorporated into the crystal structures of Mo-, and W- dichalcogenides and in PtTe2. In the former the excess metals result in the formation of metal rich mirror twin grain boundary networks, while in the latter a phase transition from PtTe2 to Pt-monotelluride can be induced. In this presentation we discuss the transformation mechanisms and the properties that arise from these compositional modifications.

5:40pm **SS+2D+AS-TuA-11 SSD Flash Poster Session: Oral Presentations***,*

5:40: SS-TuP-7 - Dr. Pierluigi Bilotto

5:43: SS-TuP-12 - Dr. Benjamen Reed

5:46: SS-TuP-13 - Mr. Xiao Zhao

5:49: SS-TuP-6 - Dr. J. Trey Diulus

5:52: SS-TuP-9 - Mr. Dustin Johnson

5:55: SS-TuP-18 - Aman Patel

Thin Films Division
Room 316 - Session TF2+2D-TuA

Low Dimension Material Application

Moderator: Mark Losego, Georgia Institute of Technology

2:20pm **TF2+2D-TuA-1 Operando and High-throughput Approaches to Advance Integrated Process Technology of Atomically Thin Device Materials***, **Stephan Hofmann**,* University of Cambridge, UK **INVITED**

For the ever increasing family of layered 2D materials many exciting properties and device concepts have been reported, yet the understanding of fundamental mechanisms that can underpin scalable process technology for these materials is lagging far behind. We developed cross-correlative operando probing capability to “unblind” the underlying mechanisms, including open and closed cell approaches for XPS, optical spectroscopy, and scanning and transmission electron microscopy. While the previous focus has been to sample select process conditions, this talk will focus on our efforts to access and fast screen the entirety of the vast, interconnected parameter space. We report on an approach to bring together substrate preparation, specifically single crystal metal catalysts, and 2D growth in a combined process flow using a standard cold-wall CVD reactor.[1] This enables large scale data acquisition and new optimisation approaches for holistic end-to-end process development, comprising growth, handling, transfer, and heterogeneous device integration for atomically thin films, particularly for emerging (opto)electronic devices where clean interfacing is crucial. We adapted a SEM to allow operando reaction monitoring for the formation and etch reactions of atomically thin WS_2 layers. This allows us to unlock a data-driven approach to understanding the underlying complex kinetics across scales. We also explored new characterization approaches for accessing pertinent device interfaces, such as TMD heterostructures,[2] and functional defects, such as emissive defects hosted in h-BN for nanophotonics, sensors, and quantum metrology and technology.[3]

[1] Burton et al., ACS Nano 14, 13593 (2020), Burton et al., submitted (2022)

[2] Schmitt et al., Nature, Accepted (2022)

[3] Stern et al, ACS Nano 13, 4538 (2019); Stewart et al., ACS Nano 15, 13591 (2021).

3:00pm **TF2+2D-TuA-3 Versatile Synthesis of 2D Superlattices from Conversion of Sequentially Layered Sub-nanomater Metal Films***, **Nicholas Glavin**[1],* Air Force Research Laboratory, Materials and Manufacturing Directorate, USA

Manipulation of bulk material properties by controlling layer-by-layer chemistry and structure of nanomaterials has remained an overarching goal of nanoscience and nanoengineering. In the case of 2D materials, heterostructures consisting of different compositions, stacking and orientation have been demonstrated leading to possibilities of artificially stacked van der Waals materials. To date, structure tunability, scalability and control of synthesis has remained a challenge. Most attempts to overcome this limitation have relied on layer-by-layer growth or transfer of grown single layers or multi-precursor growth of few-layer structures but none of these methods have the potential of scalable synthesis of controlled, periodic 2D superlattice structures.In this talk, we discuss a method to directly convert easily fabricated sub-nm metal multi-layer heterostructures on both sapphire and SiO_2 substrates followed by conversion to scalable 2D van der Waals superlattices that exhibit novel properties compared to individual 2D layers themselves including reduced bandgap, enhanced light-matter coupling, and improved catalytic performance. By annealing wafer-scale layered molybdenum/tungsten heterostructures in chalcogen vapors between temperatures of 400-800 °C, formation of mixed and horizontally-oriented superlattices as well as horizontal and vertically oriented alloys are realized. This versatility enables tunable orientation, layer structure, and chemistry in an exciting class of 2D nanomaterials and provides an opportunity to generate a wide range of artificially stacked multi-compositional 2D superlattices in controlled morphologies.

3:20pm **TF2+2D-TuA-4 Study of the Functionality of Spin Crossover Thin Films on the Ti_3C_2 Mxene Substrates***, **Saeed Yazdani**, J. Phillips,* Department of Physics, Indiana University-Purdue University Indianapolis*; B. Wyatt,* Department of Mechanical and Energy Engineering, and Integrated Nanosystems Development*; P. Wang, M. Shatruk,* Department of Chemistry and Biochemistry, Florida State University*; B. Anasori,* Department of Mechanical and Energy Engineering, and Integrated Nanosystems Development*; P. Dowben,* Department of Physics and Astronomy, Jorgensen Hall, University of Nebraska*; R. Cheng,* Department of Physics, Indiana University-Purdue University Indianapolis

Spin crossover (SCO) molecules are a class of complexes promising for use in molecular-based devices due to the change in conductance that accompanies the change in spin state by an external stimulus. Different substrates can drastically interact with SCO molecular thin films at the interface. Although metallic substrates due to their high conductance and other unique properties are points of interest to be used as substrates for many devices, they tend to lock the spin state of SCO molecular thin films near the interface due to the strong coupling between SCO complexes and high electron density on metallic surfaces. Both experimental measurements and theoretical studies demonstrated that two-dimensional (2D) surfaces have minimum interaction with SCO complexes. In this work, for the first time, the properties of SCO molecular thin films on conductive 2D Ti_3C_2 MXene are studied. Various techniques including atomic force microscopy (AFM), UV-Vis spectroscopy, and electronic transport studies are utilized to study the functionality of $[Co (SQ)(Cat)(3\text{-tpp})_2]$ SCO molecules. Conductive 2D MXene with outstanding electronic, optical and mechanical properties can be considered as an alternative substrate.

4:40pm **TF2+2D-TuA-8 AVS Thin Film Division/Graduate Student Harper Award TED-Talk Competition***,*

Vacuum Technology Division
Room 301 - Session VT-TuA

Vacuum Pumping, Leak Detection, and Modeling

Moderators: Jason Alfrey, Vacuum Technology, Inc., **Freek Molkenboer**, TNO Science and Industry, the Netherlands

2:20pm **VT-TuA-1 Design and Fabrication of Ultra-High Vacuum Test System for Quantitative Determination of Hydrogen Gettering and Permeation of Various Materials***, **Ewa Ronnebro**, R. Storms, S. Suffield,* Pacific Northwest National Laboratory*; M. Boeckmann, A. Parrot, J. Alfrey,* Vacuum Technology, Inc. **INVITED**

We will discuss a recently built state-of-the-art ultra-high-vacuum (UHV) test system with sensitive detection and quantification of hydrogen uptake, solubility and diffusion in various materials. The test system’s manifold is equipped with capacitance diaphragm gauges (CDG), residual gas analyzer, spinning rotor gauge, calibrated volumes, turbo pumps, scroll pumps and a leak detector. The manifold is surrounded by a bake-out oven to keep impurity levels sufficiently low. Two sample chambers are enclosed by high-temperature furnaces. The design was developed by Pacific Northwest National Laboratory (PNNL) in collaboration with Vacuum Technology Inc (VTI). This automated UHV system can be used for several studies of hydrogen-metal interactions including absorption/desorption kinetics, thermodynamics, isotherms, plateau pressures, isotope studies, gaseous impurity identification and permeation rate.

3:00pm **VT-TuA-3 Gas Partial Pressure Measurement by Remote Plasma Optical Emission Spectroscopy & Automated Analysis Using Artificial Intelligence***, **Dermot Monaghan**, J. Brindley, B. Daniel, V. Bellido-Gonzales,* Gencoa Ltd, UK

Vacuum deposition processes are being equipped with an ever-expanding array of sensors to gain more control over the process conditions. Unfortunately, this often presents the operator with too much data to be able to draw clear insights into the performance of the process. Machine learning algorithms are a powerful tool for analyzing large and complex sets of data and have been at the forefront of a revolution artificial intelligence. These techniques are ideally suited for analyzing problems encountered in vacuum processes, which are often expressed as “classification problems”, i.e., identifying if a leak is present in the system or not. In particular, they can be applied to the automated analysis of

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[1] **TFD Paul Holloway Award Winner**

vacuum processes by remote plasma optical emission spectroscopy (RPOES).

Remote plasma OES provides critical information on the state or condition of a process via measurement of residual gas partial pressure present in the chamber. RPOES is now a popular method of residual gas analysis (RGA), as it is industrially robust compared quadrupole mass spectrometry methods and operates from 0.5 mbar to 10^{-7} mbar. Whilst RGA information is important, expert knowledge is often required to be able to interpret the data, and in some cases, the spectra are too complex to extract key information using the human eye alone. This paper will present the application of a machine learning A.I. to the automated analysis of magnetron and remote plasma OES data. Examples include leak detection, organic contamination detection and the identification of organic molecules from cracking patterns.

4:40pm **VT-TuA-8 How Vacuum Controlled Venting Can Improve the Imagery of Electron Microscopy*, Tim Collins,*** DigiVac

DigiVac was recently approached to assist a customer with vacuum control in an electron microscope. Most electron microscopes are high-vacuum instruments, as vacuum is needed to prevent arcing and to allow the electrons to travel within the instrument unimpeded. However, the specific microscopes used by this customer have no on-board vacuum control. The user chooses between Low Vacuum and High Vacuum settings depending on the makeup of the sample being observed.

The customer observed that when using the High Vacuum setting, a vacuum level within the microscope deeper than 20 Pascals (approx. 150 millitorr) caused visible degradation in the final image. They emphasized their need to precisely control the vacuum between 20 and 30 pascals for optimal imaging. We hypothesized that raising the pressure slightly, then maintaining it, would attract the negatively charged electrons causing imaging difficulty.

Our engineering team designed a comprehensive solution using our FYRA Bleed Vacuum Controller allowing ambient air (or a connected gas supply) to be drawn into the chamber as the vacuum pump evacuates it, “balancing” the vacuum level where the user specifies. The bleed valve opens and closes using feedback control based on the current chamber pressure, measured with a separate thermocouple sensor.

Our experiments with the customer’s electron microscope showed obvious image degradation sub-20 Pascals with significant improvement when the vacuum level was strictly controlled between 20 and 30 Pascals. After some fine tuning with the built-in PID controller that is included with FYRA, we had a clearly defined SOP for alleviating the degradation issues when the vacuum level dipped below the required range. This type of bleed valve technology has a wide range of scientific applications not just in electron microscopy, but for any user looking to precisely control vacuum, introduce gasses during processing applications, or improve vacuum drying and molecular flow.

5:00pm **VT-TuA-9 Novel Cylindrical Hot Cathode Ionisation Gauge*, Ricardo A.S. Silva*,** *N. Bundaleski, O. Teodoro,* CeFiTec - Nova School of Science and Technology, Portugal

Ionisation vacuum gauges are unexpendable devices for pressure measurement in HV, and particularly UHV and XHV. However, most of their commercial realizations (e.g. Bayard Alpert gauge) are known for their lack of accuracy, mainly due to the lack of electrodes robustness and the changes in the contributions of unwanted phenomena that occur during the operation. Among the latter , the most critical are photoelectron and ion induced electron emission from an ion collector electron stimulated desorption of ions and neutrals , as well as electron backscattering from an anode [1 3]. In the present work we report a design and realization of a new hot cathode ionisation gauge aiming the suppression of these unwanted phenomena in order to obtain increased accuracy, stability and low pressure limit. In this gauge , the primary electrons form a belt like beam, following curvilinear paths in an electrode assembly resembling a cylindrical energy analyser, and end their trajectories in a Faraday cup, located inside the inner cylinder electrode [4]. The ions created by electron impact with the gas are accelerated radially towards the ion collector, practically representing one of the electrodes of the "cylindrical energy analyser". The simulations of the operation, based on a recently developed approach [5], the construction details and the first experimental tests carried out with the first and second prototypes are presented. Details of the choice of the geometry of the Faraday cup and the inclusion of a suppressor electrode on the second prototype to inhibit secondary electron emission from the ion collector are also discussed.

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[1] K. Jousten, F. Boineau, N. Bundaleski, C. Illgen, J. Šetina, O.M.N.D. Teodoro, M. Vičar, M. Wüest, A review on hot cathode ionisation gauges with focus on a suitable design for measurement accuracy and stability, Vacuum 179 (2020) 109545

[2] H. Yoshida, K. Arai, Quantitative measurements of various gases in high and ultrahigh vacuum, J. Vac. Sci. Technol. A 36 (2018) 031604

[3] I. Figueiredo, N. Bundaleski, O.M.N.D. Teodoro, K. Jousten, C. Illgen, Influence of ion induced secondary electron emission on the stability of ionisation vacuum gauges, Vacuum 184 (2021) 109907

[4] B. Jenninger et al., Development of a design for an ionisation vacuum gauge suitable as a reference standard, Vacuum 183 (2021) 109884

[5] R. Silva, N. Bundaleski, A. L. Fonseca, and O. M. N. D. Teodoro, 3D Simulation of a Bayard Alpert ionisation gauge using SIMION program, Vacuum, 164 (2019) 300 307

5:20pm **VT-TuA-10 High Performance Sealing In Extreme Environments*, Christopher Cosgrove,*** Technetics Group

This presentation details various methods of sealing to very low leak rates in extreme environments. These environments could be very high temperatures or cryogenic temperatures or very high pressures down to UHV.

Actinides and Rare Earths Focus Topic
Room Ballroom A - Session AC-TuP

Actinides and Rare Earths Poster Session

AC-TuP-1 The Underlying Simplicity of 5f Unoccupied Electronic Structure*, **JG Tobin**,* U. Wisconsin-Oshkosh*; S. Nowak,* SLAC National Accelerator Laboratory*; S. Yu,* LLNL*; P. Roussel,* AWE, UK*; R. Alonso-Mori, T. Kroll, D. Nordlund, T. Weng, D. Sokaras,* SLAC National Accelerator Laboratory

Using a simple empirical model based upon the bremsstrahlung isochromat spectroscopy of elemental Th, it is possible to explain the recent high energy resolution fluorescence detection measurements of UF_4 (n = 2) and UCd_{11} (n = 3) as well as the new inverse photoelectron spectroscopy of Pu_2O_3 (n = 5), where n is the 5f occupation number. A critical issue in this analysis is the assumption that the Th 5f states are essentially empty, which will be confirmed both experimentally and computationally. Thus, for 5f systems, this simple model provides a unified and consistent picture of 5f unoccupied density of states in simple, localized systems, as the 5f occupation varies in the early part of the series, for n = 0, ⅔, 2, 3, and 5. See References 1 and 2 for further detail.

[1] J. G. Tobin, et al., J. Vac. Sci. Tech. A 39, 043205 (2021), https://doi.org/10.1116/6.0001007

[2] J. G. Tobin, et al., J. Vac. Sci. Tech. A 39, 066001 (2021), https://doi.org/10.1116/6.0001315

AC-TuP-4 Epitaxial Actinide Heterostructures: Synthesis and Characterization*, **Kevin Vallejo**, B. May, F. Kabir, C. Dennett,* Idaho National Laboratory*; P. Simmonds,* Boise State University*; D. Hurley, K. Gofryk,* Idaho National Laboratory

Actinide-based materials possess unique physics due to the presence of 5*f* electrons. Their study has been mainly focused on their nuclear fuel applications, leaving plenty of fundamental physics aspects open for investigation. The effective examination of the unique quantum phenomena in these materials requires high purity monocrystalline samples. However, thin film synthesis of actinide compounds is particularly underexplored relative to other material systems because of limited source availability and safety regulations due to their radioactive nature. The promises, challenges, and synthesis routes for these actinide-bearing heterostructures is discussed. Molecular beam epitaxy (MBE) presents an attractive avenue for the study of actinide heterostructures because of the high degree of control over dimensionality, strain, and interfaces. Idaho National Laboratory has recently installed an MBE chamber with the specific goal of studying uranium, cesium, and thorium containing compounds. To facilitate deposition of these low vapor-pressure elements, the chamber is outfitted with a quad-pocket electron beam source, several high temperature cells, and a nitrogen plasma source. Additional studies on transition metals with complex oxidation states (Zr, Nb, Mn, Ni, and Cr) will function as surrogates for the actinide-based nitride compounds. These new capabilities will provide unrivaled opportunities for exploration of functional and energy materials with complex electron correlations, together with important experiments for model validation in computational studies.

Atomic Scale Processing Focus Topic
Room Ballroom A - Session AP-TuP

Atomic Scale Processing Poster Session

AP-TuP-1 A Computational and Experimental Investigation of Platinum Vapor Deposition Reactions on Oxygen and Nitrogen Functionalized Carbon*, I. Campbell, N. Nayir,* Penn State University*; S. Kuespert, N. Ortlieb, A. Fischer,* University of Freiburg, Germany*; A. Van Duin, **Suzanne Mohney**,* Penn State University

Nitrogen-doped carbons are useful as supports for catalysts due to their low cost, low density, and enhanced metal-support interaction. We used density functional theory (DFT) to evaluate the effects of N-doping and oxidation of graphene on the adsorption and dissociation of trimethyl (methylcyclopentadienyl) platinum ($MeCpPtMe_3$), which is commonly used for synthesizing platinum nanoparticles and films by chemical vapor or atomic layer deposition. We confirmed that oxygen incorporation in graphene via oxidation of monovacancies is thermodynamically favorable with and without N doping and discovered that N doping elongates substrate-oxygen bonds, indicating increased reactivity of the oxygen atoms bound to the substrate. According to nudged elastic band calculations, the transfer of a Me ligand from $MeCpPtMe_3$ to oxidized substrates with and without N-doping displays positive enthalpies of reaction and activation energies, making Me transfer a rate determining step. However, nitrogen doping thermodynamically and kinetically drives the Me dissociation reactions by lowering the enthalpies and activation energies of the reactions. We also showed that the dissociation of $MeCpPtMe_3$ and subsequent adsorption of Me and $MeCpPtMe_2$ on identical oxidized monovacancies is endothermic but is made exothermic by pyridinic N dopants. Thus, the adsorption and dissociation of $MeCpPtMe_3$ is expected to occur more readily on N-doped substrates than undoped ones. We also experimentally demonstrated that elevated N and O content in mesoporous carbon supports causes $MeCpPtMe_3$ to deposit more platinum but only at increased temperature (300 °C).

AP-TuP-2 Subtractive Printing of Atomic Layer Deposition using Electrohydrodynamic Jet Printing*, **Tae Cho**, N. Farjam, K. Barton, N. Dasgupta,* University of Michigan, Ann Arbor

Traditional lithography requires multiple processing steps in a resource-intensive cleanroom environment. To overcome the limitations of traditional lithographic patterning and alignment, there has been tremendous interest in developing new methods for additive manufacturing. E-jet printing is an additive manufacturing technique which allows for fast and versatile printing with high resolution. Previously, e-jet printing was used to directly deposit functional materials on the surface with solution inks. Compared to this, ALD can deposit high-quality materials with unparalleled control of film thickness and uniformity at relatively low temperatures.

Our previous work has shown that by directly printing inhibitor polymers on the surface, we can locally activate/passivate atomic layer deposition (ALD) growth for area-selective ALD (AS-ALD) [1,2]. This technique allows customizable patterns with different geometries and high resolution without the need for premade alignment masks. However, AS-ALD may suffer from defect growth and/or vapor-phase-infiltration through the inhibitor polymers which can cause undesired growth on the surface. In this study, we demonstrate the use of subtractive electrohydrodynamic jet (e-jet) printing with acid-based ink to directly pattern the metal oxides deposited with ALD.

To pattern 50 nm thick ALD ZnO that was deposited on the silicon substrate, 0.1M hydrochloric acid mixed with glycerol was used as the ink for e-jet printing. When the ink was printed, glycerol residue was left behind on the surface after ink evaporation. After soaking the sample in water, the glycerol residue was washed away with ZnO; ZnO was removed on the printed regions, exposing the underlying silicon surface. Atomic force microscopy, scanning electron microscopy, and energy dispersive spectroscopy were performed to analyze the surface topology/chemistry after patterning the ZnO layer. With e-jet, linewidth and etched depth can be precisely controlled with printing speed and the number of printed layers. This new technique can provide flexible and customizable patterning of metal oxides without the need for AS-ALD or lithography.

[1] T.H. Cho, N. Farjam, C. R. Allemang, C. P. Pannier, E. Kazyak, C. Huber, M. Rose, O. Trejo, R. L. Peterson, K. Barton, N. P. Dasgupta, *ACS Nano* **14**, 17262 (2020)

[2] N. Farjam, T.H. Cho, N. P. Dasgupta, K. Barton, *Appl. Phys. Lett.***117**, 133702 (2020)

[3] T. H. Cho, N. Farjam, K. Barton, N. P. Dasgupta, *In preparation* (2022)

AP-TuP-4 Design of Gas Flow Field for a Sustainable ALD Process Chamber*, **Kyung-Hoon Yoo**,* Korea Institute of Industrial Technology (KITECH), Republic of Korea*; G. Song,* KUMYOUNG ENG Inc., Republic of Korea*; C. Kim,* TNG Co., Republic of Korea*; J. Hwang, H. Lee,* Korea Institute of Industrial Technology, Republic of Korea*; K. Lee,* SAMSUNG DISPLAY, Republic of Korea

In order to develop a sustainable ALD process cluster tool, it is necessary to establish a manufacturing technology for a high-productivity high-efficiency ALD process chamber that reduces the intrinsic excessive consumption of energy and materials.[1] In the present study, as the part of countermeasure to the excessive consumption, a micro-gap ALD process chamber is considered for the optimized design. The changes in the flow field of nitrogen in the process space of the process chamber with the gap sizes of 1 mm and 10 mm respectively are observed at 200 ^{o}C, utilizing computational fluid CFD numerical analysis. For the present nitrogen flow field with a background pressure of 1 Torr and a temperature of 200 ^{o}C, the

Knudsen number Kn<0.1 and Reynolds number Re<<2300 are evaluated, and consequently the continuity and momentum equations of a steady-state compressible laminar flow field are considered.[2]

Acknowledgment

This work was supported by the Korean Ministry of SMEs and Startups, under Award no. S2960951.

References

[1] C.Y. Yuan and D.A. Dornfeld, 2010, *J. of Manufacturing Science and Engineering*, 132, 030918 (2010).

[2] M. R. Shaeri, T.-C. Jen, C. Y. Yuan and M. Behnia, *International Journal of Heat and Mass Transfer*, 89, 468 (2015).

AP-TuP-5 Atomic Structure Characterization of PEALE Semiconductors by Using HRSTEM, ***Chien-Nan Hsiao**, C. Chen,* National Applied Research Laboratories, Taiwan*; W. Chen,* National applied research Laboratories, Taiwan*; F. Chen,* National Applied Research Laboratories, Taiwan

An in-situ plasma enhanced atomic layer etching system has been design and fabricated. N_2O , BCl_3 and Ar plasma were used as the precursor for advanced semiconductor at various temperature. The optical detector was used to in-situ monitor the plasma spectrum during the step by step etching process. The AlGaN/GaN hetrostructure and MoS2 2D materials etching per cycle of ALE were investigated using an aberration-corrected scanning transmission electron microscope with energy distribution spectrometer. It is found that the layer by layer etching feature shows the process is a controlled self-limited reaction. The saturation curve of atomic etching rate and precursor pulsed time has been established. The etching per cycle of AlGaN is around 0.33 nm.In addition, the influence of various aberration coefficients such as defocus, astigmatism, coma, spherical aberration and star aberration on the shape of the probe and more importantly on the electron intensity distribution within the probe was calculated. The accuracy required for compensation of the various aberration coefficients to achieve sub-angstrom resolution (0.078 nm) with the electron optics system was evaluated by the calculation of phase shift. The (100) lattice spacing of MoS2 2D materials is around 0.274nm.

Biomaterial Interfaces Division
Room Ballroom A - Session BI-TuP
Biomaterial Interfaces Poster Session

BI-TuP-2 Direct Detection of COVID-19 Oligonucleotides Through Formation of Nanoparticle Satellite Conjugates, ***Hannah Umoeka**, A. Martinez, C. Afzulpurkar, M. Sharma, S. Talasila, T. Nguyen, D. Singh, I. Shortt, E. La Plante, S. Koh,* The University of Texas at Arlington

Polymerase chain reaction (PCR) and reverse transcription polymerase chain reaction (RT-PCR) have been the gold standards for accurately detecting specific oligonucleotide sequences of various pathogens such as COVID-19. However, considering the hour-long thermal cycling of PCR and RT-PCR, as well as the requirement of lab space and trained personnel, it would be beneficial to have a method that enables a rapid and point-of-care detection of a specific sequence of oligonucleotides. Here we present an approach in which a specific COVID-19 sequence is directly and rapidly detected on a small Si substrate (<1 cm^2) without any amplification. As a target oligonucleotide, we used the 67-mer DNA having the same sequence as the complementary DNA that the current CDC approved COVID-19 RT-PCR test is targeting. The target oligonucleotide is sandwiched between a capture Au nanoparticle (*C*-AuNP) and a detection Au nanoparticle (*D*-AuNP), to produce a nanoparticle satellite conjugate, where a *C*-AuNP is a 50 nm Au nanoparticle on which 20-mer capture DNA (*C*-DNA) is immobilized and a *D*-AuNP is a 30 nm Au nanoparticle on which 18-mer detection DNA (*D*-DNA) is immobilized. *C*-DNA is complementary to a portion of the target oligonucleotide while *D*-DNA is complementary to the other portion of the target oligonucleotide. The nanoparticle satellite conjugates are detected by electrically contacting the *C*-AuNP to one electrode and the *D*-AuNP to the other electrode, where an electrical current is produced when a voltage is applied between the two electrodes. The nanoparticle satellite conjugates were controllably placed on exact substrate positions using the electrostatic funneling (*Nano Lett.*, Vol.7, 439-445, 2007) and self-limiting single-nanoparticle placement (*Langmuir*, Vol.37, 11961-11977, 2021; *Appl. Phys. Lett.*, Vol.93, 073110, 2008), with self-assembled monolayers (SAMs) of 16-mercaptohexadecanoicacid and 3-aminopropyltriethoxysilane providing the electrostatic guiding structure. The total hybridization time for the assay was 10 minutes for 5 nM target COVID-19 oligonucleotides and optimization for higher sensitivity is currently underway. Our approach can be used for detection of any oligonucleotide sequence. For example, this method enabled detection of anthrax oligonucleotides by adequately changing the *C*-DNA and *D*-DNA sequences. This work was supported by the National Science Foundation (ECCS-2031770, DMR-2122128, CMMI-1463451, and CMMI-2143159).

BI-TuP-3 Study of Catechol Reaction Mechanisms*, J. Appenroth,* ***Laura L. E. Mears****, A. Celebi, M. Valtiner,* Vienna University of Technology, Austria

Redox-active catechols, in particular *L*-DOPA and dopamine, are found in many adhesive biological systems. For exmple, in marine mussels *L*-DOPA containing byssus threads are shown to adhere to different substrates in harsh saline environments. Their oxidation and reduction can be driven both by pH changes and electrochemistry. While various models have been proposed, the exact reaction paths of these catechols remain a topic of discussion.

First, we will present new insights gained on the dynamics and redox activity of catechols in aqueous solution. Their reaction paths and products were studied using electrochemistry, UV-vis and NMR spectroscopy and the results are compared to DFT based ab initio thermodynamics. To characterize the energy change during binding/unbinding events of catechols, we then show bond rupture experiments of single catechol molecules against gold surfaces using AFM and Optical Tweezers.

By combining these methods we are able to shed new light on the redox active behaviour of catechols.

BI-TuP-6 Direct Observation of Focal Adhesion by Nanoendoscopy-AFM in Live Cells, ***Alam Mohammad Shahidul**, T. Shirokawa, T. Ichikawa, K. Miyazawa, k. Miyata, T. Fukuma,* Kanazawa University, Japan

Cells are the basic building units of all living organisms. It is essential to visualize the cell structures and their dynamics at the subcellular level to understand the mechanisms of basic cellular functions. Despite the enormous efforts, there are still many things that remain underexplored about this basic unit of life. Direct imaging of such nanostructures and their dynamics inside living cells has been a great challenge. Traditional approaches including tear down the cell into various components, which may distort its natural behavior. Moreover, many nanoscale dynamics are not yet visible because of the limited resolution. Therefore, we have developed nanoendoscopy-AFM (Atomic Force Microscopy), a label-free, non-harmful imaging technique that allows us to see the intracellular structures of a living cell without breaking it apart. A long ultrathin nanoprobe is inserted into living cells to perform 2D and 3D imaging by AFM. We can visualize intra-cellular structures ranging from whole-cell to unsupported actin fibers. Further, we proved that such an imaging method based on ultrathin nanoprobes does not significantly affect cell viability. Our next aim is to investigate focal adhesions (FA) in living cells that play a crucial role in cell motility. Multiple proteins (paxillin, integrin, vinculin, etc.) form this dynamic nanostructure, which mechanically connects intracellular actin bundles to the extracellular substrate. However, it remains elusive due to the difficulties of its direct observation. We are succeeded in the direct imaging of focal adhesion in a living cell with an originally developed nanoprobe. In the future, we want to study the dynamic behavior of FAs along with TIRF microscopy which will have a significant influence on cell biology and medical sciences.

BI-TuP-8 pH Responsive Functionally Graded Nano-Composites Coatings for Studying Hepatocellular Carcinoma Cellular Behaviour, ***Juhi Jaiswal**, M. Dhayal,* Indian Institute of Technology (Banaras Hindu University), India

In the present study, a process has been developed for metal-polymer coatings on tissue culture plastic surfaces through an in-situ reduction process by chitosan. The reduction of the metal compound by chitosan was performed, thereby exploring the role of different functional moieties of chitosan in the reduction process at acidic and basic pH. Time-dependent reduction kinetics for different chitosan concentrations by monitoring the in-situ reduction of nanometal assemblies (< 10 nm) at the polymeric surface has been demonstrated to understand the role of chitosan amine and hydroxyl functional moieties in the reduction process. The FTIR spectra were used to quantify the relative change in nitrogen and oxygen atom-containing functionalities in nano-composites. ^{1}H NMR spectra of the nanocomposite were further used to identify a relative change in the corresponding peak during the interaction of different molecules in functionally graded composites. A uniform distribution of less than 10 nm nanoparticles was confirmed by TEM image analysis of composite metal-polymer coatings on a copper grid. The UV-Visible spectroscopic analysis confirmed the obtainability of tunable size, density, and functionality in composite films. XRD analysis of nanocomposite coatings confirmed the presence of nanoparticles having two (111) and (200) crystal plans. In-vitro cell viability and proliferation analysis for the HepG2 cell line was performed. These coatings can be used to develop active biomaterial for cancer therapeutics because of the existence of composite in two forms, gel and sol directed by environmental pH.

BI-TuP-9 'Plasmoresistor' Device – Electronic Transduction of Plasmon Signals for Highly Sensitive Detection of Biomolecules*, **Corbin Feit,*** University of Central Florida*; P. Rathi, S. Singamaneni,* Washington University, St. Louis*; P. Banerjee,* University of Central Florida

Sensing of biomolecules with plasmonic nanoparticles has become the "gold standard" for lab-on-a-chip devices. Observing changes to localized surface plasmon resonance (LSPR) frequency of nanoparticles provides label-free, real-time measurements without the need for chromophores or fluorophores. When a molecular binding event occurs on a plasmonic nanoparticle, the change of the local dielectric environment leads to a shift in the LSPR frequency. This optical shift in LSPR is measured via optical spectroscopy techniques such as UV-Vis or Raman spectroscopy. However, challenges to miniaturization and hardware portability remain, making point-of-care diagnostics harder to achieve.

Therefore, in this work, we present detailed results of a "plasmoresistor" sensor that monitors the photocurrent generated by hot electrons emitted from plasmonic gold nanorods. This device overcomes the limitations that arise from the above described, state-of-the-art optical readout technologies. Upon excitation of the LSPR, hot electrons are generated, transferred, and conducted through a vicinal ZnO film. Thus, the change in photocurrent (i.e., resistance) performs the sensing action. Nanoscale engineering involving area-selective atomic layer deposition is required to deposit a conductive and optically transparent ZnO, while keeping viable plasmonic nanostructured surfaces exposed for conjugation with the biomarkers.

This transformative plasmoresistor device is expected to pave the way for highly sensitive plasmonic sensors that operate through electrical detection. The use of expensive, bulky and labor-intensive instrumentation will become obsolete.

BI-TuP-10 Hemoglobin-Bound Iron Fraction In Thin Films Rapidly Solidified From 100µL Drops Measured By Extended X-ray Absorption Fine Structure (EXAFS)*, **Arjun Sekar**, A. Suresh, R. Rane, A. Thinakaran,* Arizona State University*; J. Bischoff,* Simon Fraser University, Canada*; N. Herbots,* Arizona State University*; K. Kavanagh,* Simon Fraser University, Canada

Iron (Fe) bound to Hemoglobin in blood is key to detection of anemia. Blood diagnostics(BD) via High Performance Liquid Chromatography(HPLC) require significant volumes of blood per test (8-10 mL). Such volumes lead to Hospital Acquired Anemia in a large fraction of patients(74%) [1]. Conducting BD on smaller volumes is a pressing need for modern medicine.

Recent ongoing developments of X-ray synchrotron sources and detectors with higher X-ray intensities are now making possible investigating direct EXAFS analysis on smaller blood volumes.

In this work, we use hyper-hydrophilic coatings to rapidly solidify blood drops(10-250 µL) [2], making solid state analysis feasible. Our process yields flat, Homogeneous Thin Solid Films (HTSF) in minutes without coagulation. HTSFs are sufficiently uniform, over analyzed areas (~ 5 mm^2) such that the Fe composition can be measured with an accuracy of ± 10% using conventional solid-state techniques such as X-ray Fluorescence (XRF) and Ion Beam Analysis. This is unlike conventional Dried Blood Spots(DBS). DBS are non-uniform and exhibit high fracture rates followed by detachment. In addition, Fe-rich Red Blood Cells(RBC) migrate to the periphery of DBS, while no such phase separation occurs in HTSFs [2]

We have confirmed that our process to solidify blood drops into HTSF does not modify the bonding of Fe in hemoglobin by carrying out Extended X-ray Absorption Fine Structure (EXAFS) directly on such HTSFs.

Hemoglobin is a *globular* protein, which means it folds into a spherical shape, defining bonding lengths and species surrounding Fe. Hemoglobin consists of four *heme* groups, each with an Fe bound to a *histidine* residue via N. In each *heme*, Fe is bound directly to four N nearest neighbors within a plane, with a 5th nearest neighbor and a 6th N atom. EXAFS has been reported for measurements on concentrated hemoglobin separated from whole blood and has detected oxidized Fe in hemoglobin, matching results from HPLC [3]. We carried out EXAFS at the Canadian Light Source (CLS) using fluorescence detection near the Fe absorption edge (7.126 to 7.8 keV). Our EXAFS spectra on small volume HTSF blood share similarities to previous reports on hemoglobin and consistently measure the expected Fe-N bond length of 1.97±0.02 Å [3].

Acknowledgements: CLS, NSERC, MatthewNewville

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BI-TuP-12 Detecting Shared Touch Surface Contamination with a Deep Learning-Enhanced Smartphone and Nanopatterned Material System*, **Ainslie Allen**, J. Andle, O. Biswas,* University of Maine*; R. Perry,* VEMI Lab*; S. Yasaei Sekeh, C. Howell,* University of Maine

Shared-touch surfaces can transmit diseases when not cleaned properly. Some methods of surface contamination detection exist, but nearly none are immediately accessible, hands-free, and do not require specialized equipment. This work is focused on building a deep-learning driven, smartphone-based system that interacts with nanopatterned surface appliques and identifies contamination on a surface. We used a nanopatterned material that acts as a diffraction grating and measured the difference in the refracted light pattern when the material was clean and when it was contaminated. Unlike nearly all other applications of nanopatterned diffraction gratings, our applique material is mass-produced by a Maine paper company, making it both able to be applied over large areas and affordable. The light diffracting off our nanopatterned material resulted in bright rainbows which changed significantly in intensity, length, and color composition, as measured with a standard smartphone camera, when the surface was contaminated with oil. Using this system, we were able to detect oil contamination down to a volume of 0.1µL over a surface area of 64cm2 when the data were processed manually. We then trained a convolutional neural network (CNN), ResNet 50, to detect these differences. The network was able to detect contamination at an even lower volume of 0.0001 µL over a surface area of 64cm2. Training the CNN on the collected data improved the detection performance by over 100%. Additionally, by changing the angle of the smartphone and the light source, we were able to effectively scan the surface to search for areas of contamination and under ambient light conditions, making it more applicable to use in everyday life. Adding the angle and light features into the CNN method provides extra information to the neural network and leads to a robust learning process. Together, the results demonstrate that a deep-learning-enhanced nanopatterned material system can detect general surface contamination, which may help identify potentially infectious contamination on shared touch surfaces.

BI-TuP-13 Smartphone Enabled Micro/ Nano Microscopy for Biomedical Sensing*, M. Sami,* Rutgers University*; **Umer Hassan**,* Rutgers, The State University of New Jersey

Biomarker quantification finds many applications in disease diagnostics. Detecting biomarkers require developing technologies with micro-nano sensing resolutions to enable their specific identification. Here, we report a 3D printed, portable, fluorescent microscopy system to image micro/ nano particles for biomedical applications. The 3D printed microscopy system houses an excitation source (laser diode/ LED), optical filters and lenses to achieve desired optical resolutions. The images can be taken by using a regular smartphone camera. A sample slot is housed within the platform to place the desired biological samples e.g., microparticles, or fluorescently tagged blood cells. We tested the setup using blood samples from patients at Robert Wood Johnson Hospital. We imaged leukocytes stained with nuclear stain using the platform and tested them with control microscopy instrument. We found a strong correlation between the two platforms with $R^2$of 0.99. Further, we developed a machine learning model based on artificial neural networks (ANN) to count the microparticles and blood cells in the captured images.

Lens of smaller focal lengths allow the improvement in achieving higher resolution. Further, excitation methods can also be varied for improved particles imaging performance. For sub-micron and nanoparticles imaging, we explored multiple microscopy imaging modalities including perpendicular, parallel, and slanted. We found that slanted imaging methodology where laser diode exposes the samples at various angles allows higher imaging quality and improves the nanoparticles sensing resolution and accuracy. Our system is versatile and interoperable between multiple smartphones. We tested its imaging capability using iPhone XR, Samsung Galaxy S9, Samsung Ultra S21, and Nokia Lumia. This setup can be translated for different biomarkers (e.g., cells, proteins, etc.) quantification and developing associated diagnostic products.

Chemical Analysis and Imaging Interfaces Focus Topic
Room Ballroom A - Session CA-TuP
Chemical Analysis and Imaging Interfaces Poster Session

CA-TuP-1 The Metrology Platform for in Operando Characterization of the Diamond Based High Power Devices and Detectors*, Andrei Kolmakov,* NIST

The unique electronic, physical, and thermal properties of diamond make diamond-based devices one of the most prospective for high-power electronics and detectors. The doping of diamond, however, appears to be a challenge due to high activation energy of the common p- or n-dopants. Alternative p-type doping via diamond surface hydrogenation is a key process to fabricate modern high mobility FETs.

Here we report on a simple design of the remote plasma reactor for gentle diamond surface hydrogenation. To avoid the uncontrolled surface adsorption of acceptor-like adsorbates and related band bending the design of the reactor is made as a vacuum suitcase to transfer the as-prepared device between different characterization facilities. We demonstrate the lithographic procedures and performance of the corresponding devices via measuring the properties of the electron detector and high mobility FET devices.

CA-TuP-2 Using Complimentary Characterization Techniques to Understand Interfacial Phenomena*, Vincent Smentkowski,* GE-R*; I. Spinelli, M. Knussman, M. Larson, J. Della Villa,* 1 Research Circle

Coatings and films are frequently applied to (or form on) substrate materials for a variety of reasons.Robustness of the coating is often dependent on the microstructure and/or cleanliness of the substate prior to deposition of the coating.In this presentation, we will show that the best understanding of the interfacial chemistry is obtained when multiple, complimentary, characterization techniques are used; namely scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy dispersive spectroscopy (EDS), time of flight secondary ion mass spectroscopy (ToF-SIMS), metallography, and focused ion beam (FIB).The benefits of 3D analysis will be highlighted.We will also address the limitations associated with each of the techniques.

Spectroscopic Ellipsometry Focus Topic
Room Ballroom A - Session EL-TuP
Spectroscopic Ellipsometry Poster Session

EL-TuP-2 Unraveling the Ultra-Violet Active Chiroptical Response by ZrO_2 Helical Nanostructures*, Ufuk Kilic,* *M. Hilfiker, S. Wimer, S. G. Kilic, C. Argyropoulos, E. Schubert, M. Schubert,* University of Nebraska-Lincoln

Chirality, the handedness of a material, which cannot be made superimposable on its mirror image by using simple symmetry operations (ie. translation or rotation). This symmetry breaking phenomenon has recently gained unprecedented attention due to its pivotal roles in the sub-fields of physics, chemistry, biology, and pharmacy [1]. Briefly, chiral-materials have the differential absorption properties of two possible spin states of photons: left- and right-circularly polarized light. However, the chirality of molecules found in nature is very weak and almost impossible to spectrally tailor their response. Moreover, the absorption bands of optically active chiral molecules typically appear in the deep ultraviolet part of the spectrum [2]. Using metamaterial platforms to sense these chiral molecules is challenging because majority of them are designed to operate in the infrared to visible spectral range [1,3,4]. The use of ultra-wide band gap metal oxides in the fabrication of nanostructures has been seldom discussed in the literature and investigations on their chiral properties remained almost untouched [4].

Our theoretical studies showed that one can get deep-ultra violet strong chirality response from ZrO_2 helical nanostructure design. Hence, using a recently emerging bottom-up, wafer-scale, 3D nano-morphology fabrication technique so-called glancing angle deposition, we successfully fabricated helical nano-structures from ZrO_2 ultra-wide band gap metal-oxide. By using the Mueller matrix generalized spectroscopic ellipsometry technique, the experimental chiroptical characterization was performed and verified the theoretically predicted existence of UV-active chiroptical response from the proposed ZrO_2 nanohelical metamaterial platform.

We envision that such nanostructure design with large chirality signals in the UV range of wavelengths, where the electronic transitions for biomolecules often occur can open a new avenue for their potential use in the next generation chiral sensor, bio-imaging, polarization bio-encryption or chiral-photonics device applications.

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EL-TuP-4 A Review of Refractive Index Refinements Analysis in Mono layers Absorbents Atomic Layer Deposition (ALD) or Molecular Physisorption Phenomena*, F. Ferrieu,* Optical Polarimetry Ellipsometry, Switzerland*; **Christophe Vallee,*** SUNY POLY, Albany

In situ Spectroscopic Ellipsometers (SE), is a precious real time process control tool. As frequently reported in literature, very thin layers measurements don't yield however simultaneous and uncorrelated values for the thickness t_F and the material refractive index (ri). Thickness values are highly related with the choice of an a priori assumed ri which a characteristic of the intrinsic layer's nature. The paper implements an earlier analysis of the initial Drude equations. We show that when thickness turns ultra-thin thenthe ellipsometry equations can be solved through a first order expansion in t_F. During growth, deposition or in thecase of physical adsorption on a substrate, this hypothesis is entirely fulfilled. After describing the simple way to proceed data, within Atomic Layer Deposition (ALD) examples, it is shown how few physi-sorbed monolayerscase can be handled so far. More general molecular physisorption is also considered. Particularly in theCO_2/H_2O gas adsorption inter exchange, ellipsometry turns a right method with absorbent like thin or nativesub-oxide samples. Both refractive index and thickness with high accuracy are independently reachable andwithin a rather fast acquisition capability. This will be shown in this poster.

Moreover, in vacuum chambers, the stability of alignment is just being done one time and fully optimized. A fixed physicalconfiguration inside vacuum chambers acts with benefit over usual limiting factors. An evident interest appearsin atomic layer deposition or etching as well for molecular beam epitaxy and chemical vapor depositionstechniques, and sputtering. With today's "no moving part" or "one single shot" photonic technologies,Spectroscopic Ellipsometers within this configuration can provide sensitivity more than Surface PlasmonResonance SPR which measures only the optical thickness. With the use of a limited number of wavelengths,SE exist in wide applications fields and furthermore depolarization factor acquisition gives an additionalinformation on the player building accomplishment. Since the pioneer works from H. Arwin, a large opening forbio photonics sensors appears also today. Thin silica interacting with ambient is recognized as specific adsorbents material for gases and proteins detection which is observed here in "native" oxides layers.

New Trends on Structural and Electronic Characterization of Materials, Interfaces, and Surfaces Using Synchrotron and FEL-Based Radiation Sources Focus Topic
Room Ballroom A - Session LS-TuP

New Trends on Structural and Electronic Characterization of Materials, Interfaces, and Surfaces Using Synchrotron and FEL-Based Radiation Sources Poster Session

LS-TuP-2 Synchrotron Hard X-Ray Scattering for Investigation of ALD Processes*, Jeffrey Woodward,* U.S. Naval Research Laboratory*; P. Myint, B. Jiang,* Boston University*; X. Zhang,* University of Vermont*; C. Wang, K. Ludwig,* Boston University*; R. Headrick,* University of Vermont*; S. Rosenberg,* U.S. Naval Research Laboratory*; K. Evans-Lutterodt, L. Wiegart, A. Fluerasu, R. Li, M. Fukuto,* Brookhaven National Laboratory*; C. Eddy,* U.S. Naval Research Laboratory

In recent years, synchrotron hard x-ray scattering has been increasingly utilized for *in situ* studies of atomic layer deposition (ALD) processes [1-3]. In addition to being non-destructive, sensitive to nanometer or sub-nanometer scale changes in topography or crystal structure, and providing statistical information averaged over large regions of the sample, hard x-rays are capable of penetrating the harsh process environments which preclude the use of techniques such as reflection high energy electron diffraction that are commonly used to monitor thin film growth by other methods. These advantages, combined with the high brilliance of synchrotron radiation available at modern light sources, enable the investigation of ALD growth kinetics and material properties as they evolve in real-time. This is particular useful for understanding plasma-enhanced ALD (PEALD) processes, as the plasma plays a complex role in providing both energy and reactive species through various reaction pathways, which can produce significant differences in growth behavior depending on the plasma properties.

We present an overview of various applications of synchrotron hard x-ray scattering which enable new fundamental insights into ALD processes. For each case, we highlight our studies of III-nitride semiconductor growth by PEALD conducted at National Synchrotron Lightsource II. We first discuss grazing incidence small-angle x-ray scattering (GISAXS), a highly surface sensitive technique for probing in-plane topography which is especially useful for monitoring the real-time evolution of surface islands. Next, we discuss x-ray photon correlation spectroscopy (XPCS) in a GISAXS geometry to investigate time-correlated local fluctuations about the average kinetics, or dynamics, which is made possible by utilizing a highly coherent x-ray beam. We then discuss scattering for greater incident angles, where intensity oscillations at the specular spot provide real-time information on layer thickness and surface roughness. Finally, we discuss *ex situ* grazing incidence wide-angle x-ray scattering (GIWAXS), which enables the rapid mapping of large regions of reciprocal space corresponding to interatomic distances, and is thus an extremely powerful characterization method for the myriad polycrystalline, phase change, and mixed-phase materials of interest to the ALD community.

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LS-TuP-3 High Energy X-Ray Photoelectron Spectroscopy of COTS Electronics Interfacial Failure Modes*, Samantha G. Rosenberg,* *M. Meyerson, M. Kottwitz,* Sandia National Laboratories*; R. Rajendran,* Georgia Institute of Technology*; M. Reingold, B. Young,* Sandia National Laboratories*; P. Singh, J. Kacher,* Georgia Institute of Technology*; J. Fowler,* Sandia National Laboratories

The increasing complexity and miniaturization of electronics have driven demands to lean heavily on commercial off the shelf (COTS) electronics parts. COTS part defects are typically stochastic, making root cause identification challenging when failures occur. This study aims to identify a novel characterization scheme which can uncover fundamental relationships between interfacial material defects and chemical and physical phenomena which drive ultimate failure of COTS parts in relevant field environments. We first apply accelerated stress testing in corrosive environments using salt-fog chambers and environmental chambers to identify marginal or defective parts and then characterize these parts to identify corresponding (electro)chemical phenomena. Characterization includes studying the local electric field around the parts with scanning vibrational electrode technique (SVET) and examining latent and emerging defects in the COTS parts using in-situ liquid cell transmission electron microscopy (in-situ TEM) to correlate and predict interfacial material properties with electrochemical phenomena in relevant field environments. HAXPES will then allow for identification of subsurface chemistry related to metal migration, metal precipitate, and corrosion product formation due to exposure in various accelerated aging experiments performed before beamtime exposure using the aforementioned techniques.

Sandia National Laboratories is a multi-mission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

LS-TuP-4 Insitu AFM Imaging of the Structural and Morphological Evolution of Epitaxial $LiCoO_2$ Films during Charge and Overcharge*, Yingge Du,* Pacific Northwest National Laboratory*; W. Samarakoon,* Oregon State University*; J. Hu, L. Wang,* Pacific Northwest National Laboratory*; Z. Feng,* Oregon State University*; J. Tao,* Pacific Northwest National Laboratory

Capacity decay of layered cathodes in high voltage applications underscores the need to utilize accurate and precise techniques to understand the underlying mechanisms. Here, we use well-defined epitaxial $LiCoO_2$ (LCO) films on $SrRuO_3/SrTiO_3$ (SRO/STO) with controlled orientations and defect structures along with *in situ* electrochemical atomic force microscopy to probe the structural and morphological evolutions during the charge and overcharge processes. We quantitatively show the morphological changes in both reversible delithiation regime and irreversible over-delithiation regime, and correlate the overall electrochemical behaviors to atomic scale defect evolutions in the films. We also observe a significantly lower charging capacity for LCO/SRO/STO(111) compared to that of LCO/SRO/STO(001) films of the same thickness, which is ascribed to the different types of atomic scale defects formed during the film growth process.

Magnetic Interfaces and Nanostructures Division
Room Ballroom A - Session MI-TuP

Magnetic Interfaces and Nanostructures Poster Session

MI-TuP-1 Microscopy with Momentum and Imaging Spin-Filter (Au/Ir)*, Marten Patt,* *M. Escher, N. Weber, T. Kuehn, M. Merkel,* FOCUS GmbH, Germany

Momentum Microscopy is a new technique in surface science, in which the momentum (or the real-space) distribution of photoelectrons is projected onto an image plane by using a photoemission electron microscope (PEEM) column. In case of momentum imaging the k_x-k_y plane can be energy-filtered by a double-hemispherical electrostatic analyzer (IDEA) to achieve a monochromatic momentum distribution. The ability of the method to map the complete angular distribution of photoelectrons is quite successfully used for photoemission orbital tomography (e.g. at the NanoESCA in Trieste [1]). An innovative extension of this technique is to use the monochromatic electron distribution behind the double-hemispherical analyzer for 2D imaging spin-filtering. Early experiments with a NanoESCA were performed with a W(100) single crystal as electron-mirror with spin-polarization dependent reflection [2], but only the step to a Au passivated Ir (100) single crystal with long-term stable scattering properties paved the way to a broadly based scientific useability.

We will show results from our two first commercial Au/Ir 2D Imaging Spin Filters. Pre-characterizations of the Au/Ir crystal were done with LEED and a Ferrum-Detector setup [3] to find optimal preparation conditions and scattering energies for a high single-point figure-of-merit (with Sherman function >60% and Reflectivity >1%) [4]. Spin-filtered images of magnetic domains show that along the diameter of the field of view (e.g. 36 µm) more than 100 separate image points can be resolved. This increases the effective 2D figure-of-merit of this spin-filter by nearly four orders of magnitude compared to single-channel spin-detectors.

MI-TuP-2 Investigating the Magnetic Properties of the Co-Tb Phase Diagram*, Sydney Harrington,* *B. Wilfong,* United States Naval Academy*; D. Heiman,* Northeastern University*; M. Jamer,* United States Naval Academy

There has been recent interest in Co-Tb compounds for its potential use in various spintronic applications, since it has been shown to display spin-orbit torque while maintaining a low magnetic moment. While spintronic devices have been made from ferromagnetic materials, the low moment properties have been enticing for researchers since it will enable devices to become more efficient, perform at high speeds, and less corruptable. Compounds made from Co-Tb are especially interesting since Tb and Co combine a 4*f* and 3*d* orbitals, which allows for interesting magnetic coupling causing for a net magnetic moment or angular momentum to go to zero. The 3*d*-4*f* interactions are interesting to study since rare-earth elements normally have a large moment and large coercivity associated with hard ferromagnets and when a 3*d* transition element is added, these materials have an unpredictable magnetization properties.

The Co-Tb system has been shown to be advantageous in a variety of low-moment ferrimagnetic applications. In previous work, it was found that the Co-Tb system is ideal for potential spin-orbit torque with overall low-magnetization at room temperature. While various studies have shown the properties of the compound, there was not much known about the structure due to the amorphous nature in thin films. In our work, we have synthesized bulk ingots of Co-Tb in a variety of stoichiometric ratios and found that the Co_7Tb_2 is the phase responsible for the low-moment properties in various works. Through the structural and magnetic investigations of multi-phase ingots, we have determined the magnetic properties hexagonal and rhombohedral polymorphic phases of the Co_7Tb_2 structure and the effect of the other binary phases on the interfaces on the desired phase.

MEMS and NEMS Technical Group
Room Ballroom A - Session MN-TuP
MEMS and NEMS Poster Session

MN-TuP-1 Nanoelectromechanical Resonators Based on Mechanically Anisotropic 2D Material*, Bo Xu*[1], *F. Xiao, J. Zhu, Y. Liang, C. Jiao, J. Li, Q. Deng, S. Wu, T. Wen, S. Pei, J. Xia, Z. Wang,* University of Electronic Science and Technology of China

The rich properties of atomic layer crystals enable researchers to design and fabricate micro/ nanoelectromechanical devices and systems towards signal processing and sensing applications. In particular, mechanical properties of two-dimensional (2D) materials play an increasingly important role in designing devices with predictable responses in order to achieve desired device performance, such as frequency and mode sequence in 2D nanoelectromechanical systems (NEMS) resonators.

Rhenium disulfide (ReS_2) crystal is a 2D semiconductor with weak interlayer coupling which can lead to relatively low Young's modulus (E_{Yz}=0.4 GPa) along the out-of-plane direction of the layered crystal. Interestingly, it exhibits strong in-plane anisotropy. However, its mechanical anisotropy has not been experimentally demonstrated yet. Here, we experimentally demonstrate ReS_2 nanomechanical resonators, and elucidate their mechanical anisotropy using multi-mode spectromicroscopy measurements.

ReS_2 nanomechanical resonators are fabricated by mechanically exfoliating MoS_2 crystal onto Si/SiO_2 substrates with pre-patterned cavities and electrode. We measure the multi-modal resonance response using a customized scheme that incorporates electrical driving and optical detection. For each resonance peak, by using XY stage and spectromicroscopy measurement scheme, we can visualize the mode shape. We then perform extensive calculations to fit to the experimental results. Specifically, we sweep the input parameters (E_{Yx} and E_{Yy}) in an FEM model for an anisotropic circular drumhead resonator, and pinpoint the optimal input parameters by minimizing the collective difference between measurement and calculation for all modes.

The thickness t and diameter d of the ReS_2 resonator are t =106 nm and d =10 µm. The frequency response of first six vibrational modes are shown in the Figure, respectively. Using the spectromicroscopy technique [8], the mechanical vibration modes shapes are visualized. We then run numerical simulations (using both mechanically anisotropic and isotropic models) to predict multimode response and mode shape of the ReS_2 resonator, and optimize the input Young's moduli to achieve the best agreement between measurement and simulation results. We find that the best result is produced by the mechanically anisotropic model, with E_{Yx}= 191 GPa and E_{Yy}=134 GPa for our ReS_2 device. We thus quantitatively determine the mechanical anisotropy in ReS_2.

In summary, we clearly prove that ReS_2 is mechanically anisotropic, and successfully obtain its Young's moduli.

Figures and Refs in PDF.

MN-TuP-2 Frequency Scaling in Electrically Tunable WSe_2 Nanomechanical Resonators*, Jiankai Zhu*[2], *B. Xu, F. Xiao, Y. Liang, C. Jiao, J. Li, Q. Deng, S. Wu, T. Wen, S. Pei, J. Xia, Z. Wang,* University of Electronic Science and Technology of China

Nanomechanical resonators based on atomic layers of tungsten diselenide (WSe_2)show good promises for ultralow-power signal processing and novel sensing functions. However, frequency scaling in WSe_2 NEMS resonators remains yet to be explored, which impedes the realization of 2D circuits involving WSe_2 resonators at large scale. Here, we elucidate frequency scaling law in such 2D semiconducting resonators, and determine that the Young's modulus of WSe_2 is 130GPa. Further, by operating devices from the appropriate mechanical region, we demonstrate a broad frequency tuning range (up to 230%) with just 10V gate voltage, representing some of the highest gate tuning efficiency in 2D NEMS resonators reported to date.

We fabricate a total of 26 circular drumhead WSe_2 resonators of different diameters using mechanical exfoliation and dry transfer technique, with device thickness ranging from single layer to 127 layers. We measure the resonant response of WSe_2 resonators using a custom-built 2D resonator measurement system based on laser interferometry, in which the device's vibratory motion is transduced into optical signal and detected by a photodetector.

From measured data of all the devices, we determine that the Young's modulus E_Y of WSe_2 is 130GPa, in good agreement with theoretical predictionsand nanoindentation measurements, as well as the pre-tension to be 0.05-0.4N/m, in good agreement with other measurements.

We further analyze the frequency scaling and elastic transition of WSe_2 resonators. From the experimental data, we clearly observe the elastic transition from the "membrane" limit (left end) to "plate" limit (right end) in different devices, allowing us to fully explore resonant characteristics by leveraging the unique mechanical responses from each specific region. For example, we observe that devices with lower pre-tension see a greater relative change of total tension, and thus exhibit larger relative frequency shifts. We therefore choose the 8 µm-diameter, 18.4 nm-thickness device to demonstrate efficient gate tuning. This NEMS resonator exhibits clear and consistent gate tuning of frequency under three measurement schemes: electrical excitation, optothermal excitation, and thermomechanical resonance. We achieve an excellent tuning range $\Delta f/f_0$ reaching 230%, comparable to the best performance found in NEMS resonators, as well as a gate tuning efficiency of 23%V^{-1}, the highest among 2D NEMS resonators reported to date. Our resultsoffer important design guidelines for frequency tunable NEMS resonators based on these emerging 2D materials.

Fig & Ref in PDF

MN-TuP-3 Strain-Modulated Dissipation and Signal Transduction in Two-Dimensional Molybdenum Disulfide Nanoelectromechanical Resonators*, Pengcheng Zhang*[3], *Y. Rui,* Shanghai Jiao Tong University, China

Resonant nanoelectromechanical systems (NEMS) based on two-dimensional (2D) materials such as molybdenum disulfide (MoS_2) are interesting for highly sensitive mass, force, photon, or inertial transducers, as well as for fundamental research approaching the quantum limit, by leveraging the mechanical degree of freedom in these atomically thin materials. For these mechanical resonators, the quality factor (Q) and signal transduction are essential, yet the mechanism for energy dissipation and accurate signal transduction model in 2D NEMS resonators have not been fully explored. Here, we present the accurate strain-modulated dissipation model and equivalent circuit model focusing on NEMS resonators based on a 2D semiconductor: MoS_2. We further show that for doubly-clamped resonators, the Q increases with larger DC gate voltage, while fully-clamped drumhead resonators show the opposite trend. Using DC gate voltages, we can tune the Q by ΔQ/Q = 120% for fully-clamped resonators, and by ΔQ/Q = 229% for doubly-clamped resonators. We develop the strain-modulated dissipation model for these 2D NEMS resonators, which is verified against our measurement data for a fully clamped resonator and a doubly clamped resonator. We find that static tensile strain decreases dissipation while vibration-induced strain increases dissipation, and the actual dependence of Q on DC gate voltage depends on the competition between these two effects, which is related to the device boundary condition. Furthermore, we find that strain also tunes the mobility and carrier density of MoS_2, and develop a strain-modulated equivalent circuit model for 2D MoS_2 NEMS resonators, to show the

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[1] **MEMS/NEMS Best Research Work Award**

[2] **MEMS/NEMS Best Research Work Award**

[3] **MEMS/NEMS Best Research Work Award**

enhancement of signal transduction efficiency due to the strain effect. Such strain dependence is useful for optimizing the resonance linewidth and signal transduction efficiency in 2D NEMS resonators towards low-power, ultrasensitive, and frequency-selective devices for sensing and signal processing.

MN-TuP-4 Titania Nanotube Array Electrochemical Characterization and Integration Into a Mechanically-Adaptive Neural Interface*, D. Sacco, H. Wang, T. Stegall, A. Menon, Y. Yang, J. Capadona,* Case Western Reserve University*; H. Amani Hamedani,* ***Allison Hess-Dunning****,* Louis Stokes Cleveland VA Medical Center

Optimizing the functional performance and lifetime of implanted biosensor technologies requires close integration and interaction at the biotic-abiotic interface. Devices that penetrate into tissue (e.g., intracortical neural interfaces) evoke biologically-mediated responses that isolate the device from the tissue and inhibit biosensing capabilities. Two materials strategies used to promote device integration with local tissue are 1) mechanically-compliant structural materials that reflect the mechanical properties of biological tissues, and 2) nanostructured materials that reflect the scales at which cells and proteins interact. Functional devices for biosensing are typically heterogeneous systems comprised of multiple materials that each serve a purpose (e.g., structural vs. functional, conductive vs. insulating), suggesting that multiple strategies are needed within the same implanted device to improve integration with tissue.

Our team has augmented our previous mechanically-adaptive, polymer nanocomposite (NC) neural interfaces with nanostructured titania nanotube arrays (TNAs) as the sensing electrode material. TNAs are vertically-oriented, highly-organized arrays of nanoscale-diameter open-ended tubes that form from titanium in an electrochemical anodization process and have previously been shown to promote tissue integration. Implementing this dual-faceted approach to improving neural interfaces required 1) that the TNAs have a sufficiently low electrode-electrolyte impedance of $<20\ \Omega\cdot cm^2$ at 1 kHz to facilitate sensing, and 2) a fabrication process to produce a functional device that incorporates TNA microelectrodes into the soft NC substrate. Electrochemical impedance spectroscopy was used to characterize a series of as-anodized and post-treated TNAs. The impedance magnitude and variability across a sample were heavily influenced by the processing conditions, with annealing at 450°C yielding the lowest impedance. Plasma-based surface modification lowered the impedance of samples by up to 83%, thereby bringing them into an acceptable impedance range. An inverted microfabrication process for integrating TNA microelectrodes into the NC structure was developed using a combination of photolithography and laser micromachining to produce a functional device with six layers in a four-photomask process. We expect that the improvements in integration with biological systems afforded by the combined tissue response mitigation strategies will enable the long-term, high-quality performance needed for advancing neuroscience and clinical brain-machine interfaces.

MN-TuP-5 One-Dimensional Photonic Crystals with Narrow-Band Defect Modes Fabricated by Direct Laser Writing*,* ***Victoria P. Stinson****, M. McLamb, T. Hofmann,* University of North Carolina at Charlotte

The ability of two-photon polymerization to fabricate high contrast one-dimensional photonic crystals for the infrared spectral range has been demonstrated [1]. In general, photonic crystals induce a reflective photonic bandgap where transmission is forbidden. This is achieved by creating a dielectric periodicity in one-, two-, or three-dimensions [2]. One-dimensional photonic crystals create a dielectric periodicity in a single direction. These photonic crystals can be easily tuned to the desired spectral range by altering the geometrical structure. The introduction of defects which disrupt the dielectric periodicity of these one-dimensional photonic crystals can induce narrow band transparencies within the photonic bandgap. This spectral effect has recently been demonstrated in one-dimensional photonic crystals fabricated by two-photon polymerization [3]. Photonic crystals with defects show an increased sensitivity to layer thickness non-uniformity. For this presentation we will further analyze the sensitivity these photonic crystals have to this important fabrication parameter and discuss potential applications.

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MN-TuP-6 Ultra-High-Quality-Factor Membrane Resonators for Gas Pressure Sensing*,* ***Christoph Reinhardt****,* Deutsches Elektronen-Synchrotron (DESY), Germany*; H. Masalehdan,* University of Hamburg, Germany

Nanomechanical resonators are chip scale implementations of a mechanical oscillator, which are of both practical and fundamental interest. In many applications, such as force sensing and quantum control of mechanical oscillators, it is typically advantageous to create lightweight, compliant mechanical elements with high quality factors Q. Recent years have seen a rapid development of devices with ever higher Q values, with current records approaching Q~10^{10} at room temperature. As a result, these devices become increasingly sensitive to smallest changes in certain environmental parameters, such as the pressure of the surrounding gas. In this work, we demonstrate the practical use of a mm-scale nanomechanical trampoline resonator with intrinsic resonance frequencies $f \sim 100$ kHz and $Q \sim 10^7$ for gas pressure sensing. To this end, we place the trampoline inside an ultra-high-vacuum chamber and interferometrically measure resonance frequency and quality factor of its fundamental out-of-plane mode as a function of gas pressure, using air and helium. In the pressure (p) range from 10^{-6} mbar to 10^3 mbar (i.e., ambient pressure), the quality factor continuously decreases from 10^7 to 15 (30) for air (helium). At ~ 10 mbar we observe a change from a Q~p^{-1} to a Q~$(1+a\sqrt{p})^{-1}$ dependency, with fit parameter a, related to a transition from the free molecular to the viscous flow regime. This transition is accompanied by the onset of a decrease in the trampoline's resonance frequency towards higher pressures. Leading to a 10 % (3 %) reduction at ambient air (helium) pressure. We find excellent agreement within ~ 10 % between the measured data and a model, covering the investigated pressure range. Based on additional measurements for higher-order modes, we argue, that the estimated deviation might be mainly limited by a commercial reference pressure gauge. In this regard, we discuss prospects for nanomechanical-resonator-based pressure sensing with a precision on the order of few percent and the inherent benefit of self-calibration. In addition, we highlight the possibility for extending the measurement range with optimized devices by more than two orders of magnitude towards both lower and higher pressure ranges.

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MN-TuP-7 The Effect of Laser Processing on Drug-Loaded Polymers for Microfabricated Neural Interfaces*,* ***Natalie Mueller****, M. Ya Mungu Ocoko, D. Chirra, P. Dernelle, A. Hermoso, J. Capadona, A. Hess-Dunning,* Case Western Reserve University

Drug-loaded polymers can be used in a multitude of biomedical applications, including drug-eluting, polymer-based intracortical microelectrodes to mitigate the neuroinflammatory response (Fig. 1). While these devices have shown promising results in reducing neuroinflammation around the microelectrode implant site, fabrication processes can affect the therapeutic efficacy of the drug. In our device, we load a polymer (polyvinyl acetate) substrate with the antioxidant/anti-inflammatory natural product, resveratrol. Resveratrol undergoes transformation from its more therapeutic isomer trans-resveratrol to its less potent form cis-resveratrol when exposed to heat and UV light. During our microfabrication process to integrate functional recording electrodes (Fig. 2), the resveratrol-loaded polymer substrate is exposed to both heat and UV light, particularly during the laser-micromachining step to create individual devices. We hypothesized that a higher power and laser path density would facilitate the conversion of trans-resveratrol to cis-resveratrol. Trans- to cis- conversion can be detected through a decrease in the absorbance peak in UV-vis spectrophotometry, as cis-resveratrol has a lower absorbance wavelength (287 nm) than trans-resveratrol (306-317 nm).

To test the effect of laser-micromachining on the resveratrol-loaded polymer devices, we first cut unloaded and resveratrol-loaded polymer substrates with 6 different combinations of laser power and geometry (Fig. 3). The cut devices were then incubated in 1X PBS, in which the hydrated state of the polymer allows the loaded resveratrol to elute from the sample to determine resveratrol release rate. The incubation solution was measured using UV-vis spectrophotometry at set time points (Fig. 4). The resveratrol release profile suggests that resveratrol-loaded polymer samples with a higher laser path density release more resveratrol (Fig. 5). Laser power did not strongly impact the peak absorbance or wavelength at peak absorbance. However, higher laser power corresponds to a less precise cut and increased damage to the resveratrol-loaded polymer substrate (Fig. 6). Samples with a higher laser path density (100 µm-wide serpentine, 200 µm-wide serpentine) have a lower wavelength at peak absorbance compared to samples with a lower laser path density (rectangular, 1000 µm-wide serpentine), which could be attributed to changes in the polymer, resveratrol form, or both. Together, these results inform the loading parameters for resveratrol-loaded polymer substrates, the fabrication process parameters to optimize active molecule release, and interpretation of the histology data from *in vivo* studies.

MN-TuP-8 Pressure Control During Bronze Infiltration of Binder-Jet Printed Stainless-Steel to Create Metal Microchannels*, H. Davis, J. Harkness, I. Kohls, N. Crane, B. Jensen, R. Vanfleet,* ***Robert C. Davis****,* Brigham Young University

Additive manufacturing (AM) of metal microscale channels could enable microfluidic applications requiring higher temperature and higher thermal conductivity materials. Combining these thermal properties with AM's ability to form small-scale complex flow paths could create functional structures like microscale gas chromatography columns or heat exchangers. We are developing processes to fabricate sealed metal microchannels using bronze infiltration of binder-jet printed stainless-steel parts. In this approach, bronze infiltrant must fill the porous material produced by binder jetting without filling the formed microchannels. This was achieved using pressure control reservoirs, wherein the powder filled reservoirs (pore size ~60 µm) are used to control infiltrant pressure. With pressure control, the infiltrant selectively filled the small pores between particles in the printed part (pore size ~3 µm) while leaving formed microchannels (200 to 900 µm) empty.

Manufacturing Science and Technology Group
Room Ballroom A - Session MS-TuP

Manufacturing Science and Technology Poster Session

MS-TuP-2 Materials Metrology Using in-Line SIMS System for Improved Manufacturing Process Control in Advanced Nodes*,* ***Ganesh Vanamu****, J. Hoffman, L. Rooney, S. Okada,* Nova Measuring Instruments

As the semiconductor industry transitions more rapidly towards advanced technology nodes, devices are getting more complex and process challenges are increasing dramatically. Moreover, an abundance of new materials requires inline control of critical parameters, such as composition, dopant, thickness and local variations within the device.

For example, Germanium content in SiGe correlates to channel stress, and the Ge fraction has been increasing steadily as technology rapidly advances towards 3D structures. When stress is high, epi layers can suffer from multiple problems such as defect formation, facet formation, non-uniform strain. To enable process control on the Ge%, and Boron doping concentration in the complicated SiGeB epi stacks is critical in high-volume manufacturing (HVM), and there is no single in-line metrology technology that can perform the measurement.

Ion implantation, mainly Boron, Phosphorous, and Arsenic, has a long history of use in semiconductor manufacturing. After implantation, the concentration distribution of the implanted ions within the material will resemble a Pearson IV distribution., Secondary Ion Mass Spectroscopy (SIMS) is the only metrology method capable of measuring the peak concentration, peak depth, and dose simultaneously.

Contamination introduced during semiconductor processing is another critical concern because it can degrade device performances and can eventually cause device failures. Contaminants like Chlorine (Cl– ions) cause Al-Cu corrosion and metal cross- contamination in integrated circuits that could lead to wafer scraps. Integration and reliability issues can result from diffusion of Fluorine into underlying films or substrates. Therefore, there is a need for in-line monitoring of these contaminants.

The metrology goal is to enable automated in-line measurements that can be used for process monitoring of material concentrations, with vertical resolution. This paper explores the use of in-line SIMS technology, enabling depth profiles of the materials composition in the critical deposition steps in HVM, previously limited to a lab environment. This paper describes how in-line SIMS can be used to measure SiGe epi material composition profiles (such as thickness, Ge% and Boron concentration) as a function of depth. This study also shows measurements of peak concentration, peak depth, and dose of Boron implantation simultaneously to provide better implant process control. This paper also evaluates the detection sensitivity levels of contaminants like C, F, Cl in positive and negative ion mode with an Oxygen primary ion beam, as well as the use of proxy species or alternate isotopes for improved results.

Nanoscale Science and Technology Division
Room Ballroom A - Session NS-TuP

Nanoscale Science and Technology Poster Session

NS-TuP-1 Collection of Raman Signal in a Liquid Using Plasmonic Vortex Fiber*,* ***Rohil Kayastha****, B. Birmingham, Z. Zhang,* Baylor University

Tip-enhanced Raman spectroscopy (TERS) has been demonstrated to achieve nanoscale resolution by focusing the light beam at the tip directly from the free space using the surface plasmon polariton (SPP). Conventional TERS applications possess problems such as low excitation and collection efficiency, optical alignments, and so on. Application of TERS in a liquid environment exposes additional challenges because of difficulty in focusing the excitation beam as the beam diffracts at the air-liquid interface between different refractive indexes. Here, a plasmonic fiber-based TERS, using SPP in a conical Kretschmann configuration, nano-focuses the radially polarized beam at the tip apex to excite and uses the back-collection method to collect the Raman signals to overcome the aforementioned challenges.

A tapered fiber was gold (Au) coated to be used as the plasmonic tip for TERS. Both linear and radial polarized beams can plasmonically excite into SPP mode at the tapered region, however, only a radial polarized mode can be localized without destructively interfering which achieves nano-focused light at the tip apex. Therefore, vortex fiber, a polarization-maintaining optical fiber, was used to guide the radially polarized mode. The plasmonic excitation of vortex fiber with internal illumination of the radially polarized beam was studied to demonstrate nano-focusing of the light beam near the tip apex using a liquid sample. The concentration dependence of the plasmonic coupling in the liquid sample was demonstrated. The Raman signal displayed dependence on the refractive index of the liquid as the concentration of the solution changed. Stronger Raman signals at the air-liquid interface were observed in comparison to when the fiber tip was fully submerged into the liquid which is due to the combination of the coupling of the waveguided mode from the fiber to the SPP mode and to a waveguided mode in the tapered liquid layer that forms over the tip. The air-liquid interface experiment also demonstrates that most of the signal is obtained near the tip apex than from the shaft of the probe. The plasmonic tip has been incorporated into a near field scanning optical microscope (NSOM) to obtain the topographical and spectroscopic information on a substrate with nanoscale resolution. The polarization dependence of the light beam (radial and azimuthal polarization) will also be tested to compare and understand the plasmonic coupling to enhance the coupling efficiency thus, enhancing the Raman signal.

NS-TuP-2 Chemical Mechanical Planarization Slurry Stability Study*,* ***Yibin Zhang****,* FUJIFILM Electronic Materials USA., Inc.

The stability of slurry for Chemical Mechanical Planarization (CMP) is one of the big concerns in semiconductor fabs. It might potentially be a deal-killer for its application due to its short period of stability even though it has a good performance in other aspects, like removal rate, erosion, and dishing. one of the main reasons for defectivity, an important factor of slurry performance in the CMP process, is the presence of large agglomerates in the slurry. As a result, lots of efforts have been done to stabilize of slurry and formulate highly stable slurries, which minimize the formation of oversize agglomerates. A highly stable CMP slurry is critical to reduce process-dependent defectivity such as scratches and particle residues.

In this work, we present a novel optical technique, MultiScan Emulsion and Dispersion Stability Analyzer, which can efficiently and accurately check the stability of certain formulations of the slurries or screen raw materials and their combination's stability. A few samples will be analyzed to demonstrate the capability of stability investigation by using this technique. In the meantime, the traditional stability test method will be used as well for comparison. We propose some mechanisms respectively for stability for each sample. This technique will save >50% time for routine shelf-life stability study compared to the traditional test method.

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NS-TuP-3 A New Tool for Quantum and Nanoscale Materials Engineering*, Gianfranco Aresta,* Ionoptika Ltd, UK

Quantum computing is the next great frontier of science. It has the potential to revolutionise many aspects of modern technology, including digital communications, “quantum-safe” cryptography, as well as incredibly accurate time measurements.

Single impurity atoms in semiconductors are receiving attention as potential quantum technologies, and proof-of-concept devices have shown promise. However, such devices are incredibly challenging to manufacture, as single atoms must be placed within ~ 20 nm of each other within a pure ^{28}Si matrix.

All working devices thus far have been fabricated using hydrogen lithography with an STM followed by atomic layer deposition. It is labour-intensive and requires several days of meticulous preparation to create just a single quantum bit (qubit). Real-world devices will require arrays of hundreds or thousands of impurity atoms, highlighting the requirement for a scalable method of positioning single atoms with nanometre precision.

We report on a new commercial instrument for the fabrication of quantum materials and devices via ion implantation. A well-established technique in the semiconductor industry, ion implantation is both flexible and highly scalable. The instrument features a high-resolution mass-filtered focused ion beam (FIB), a high-sensitivity deterministic implantation system, 6-inch wafer handling, and a high-precision stage.

The ion dose delivered to the sample can be adjusted across a wide range, providing several materials engineering capabilities in a single tool. The deterministic implantation system allows single ion implantation with confidence levels as high as 98%. Operating in a high beam current mode provides direct-write capabilities such as isotopic enrichment and targeted ion-implantation of nanomaterials such as nanowires and graphene.

The liquid metal ion source and mass filtered column can implant many different elements with isotopic resolution. Available sources include silicon, erbium, gold, and bismuth, while many others of technological interest are in development.

NS-TuP-4 Atomic Silicon Wires: Dopant Mediated Charging Characterization*, Max Yuan,* University of Alberta, Canada*; R. Wolkow,* University of Alberta, Quantum silicon, Canada*; R. Achal, J. Croshaw,* Quantum Silicon, Canada*; T. Chutora, F. Altincicek, C. Leon,* University of Alberta, Canada*; L. Livadaru,* Quantum silicon, Romania*; J. Pitters,* Quantum silicon, Canada

CMOS technologies are approaching their performance limits. Atomic silicon electronics are poised to provide the next-generation of devices. This beyond CMOS platform consists of exactingly patterned dangling bond (DB) circuitry on hydrogen passivated silicon (H-Si).[1] Many passive and active components can be made of DBs, here we investigate atomic silicon wires. We employ a recent dopant based charge sensing procedure in conjunction with non-contact atomic force microscopy to study the charging behavior of atomically fabricated DB wires on H-Si (100) 2x1. On its own, this method can be used to rapidly detect local net charge with single electron sensitivity; coupled with AFM, it can drastically improve confidence in data interpretation.[2] In this scheme, a single DB sensor is employed to detect a sharp step in its I(V) spectroscopy due to the ionization of a nearby arsenic dopant. As charged DBs are fabricated nearby, local band bending shifts the dopant ionization voltage which can act as a charge sensor. Wires, both parallel and perpendicular to the dimer direction were systematically lengthened and studied using this method. The charging behavior for various lengths of wire, and novel observations, such as a length dependent flip flop in electron occupation for perpendicular wires are demonstrated. This method and these results will be used to improve the characterization of DB structures and will eventually be directly compared to theory to improve the modeling of DB circuitry.

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Plasma Science and Technology Division
Room Ballroom A - Session PS-TuP
Plasma Science and Technology Poster Session

PS-TuP-1 SiO_2 Contact Hole Etching Using Heptafluoropropyl Methyl Ether Plasmas*, Sanghyun You,* *C. Kim,* Ajou University, Republic of Korea

Perfluoro carbons (PFCs) such as CF_4 and c-C_4F_8 are mainly for SiO_2 etching. PFCs aggravate global warming even in small amounts due to their high global warming potentials (GWPs). As the critical dimension keeps decreasing, the number of processes consisting of etching-deposition repetition such as double patterning technology increases, leading to an increase in PFC emission. According to the World Semiconductor Council, the emission of PFCs from the global semiconductor processes in 2020 has been increased by 37.9% compared to that in 2012. Semiconductor industries are trying to reduce PFC emissions through post-treatment processes such as recovery or decomposition of exhaust gases. However, it is not suitable as a long-term solution since a lot of electricity or water is used in the post-treatment processes. To reduce PFC emission from a long-term perspective, it is necessary to develop a process using materials with low GWPs. Unsaturated fluorocarbons, iodofluorocarbons, fluoroethers, and fluoroalcohols have been studied as alternative chemistries to PFCs.

In this study, SiO_2 contact hole etching was conducted using heptafluoropropyl methyl ether (HFE-347mcc3) plasmas. HFE-347mcc3 belongs to fluoroethers, and its GWP (~350) is significantly lower than that of PFC. The angular dependence of the SiO_2 etch rates were investigated to explain the etch mechanism during SiO_2 contact hole etching.

PS-TuP-2 Selective Cyclic Etching of Silicon Oxide Over Silicon Nitride Using NF_3/H_2 Remote Plasma and NH_3*, Hong Seong Gil,* *Y. Gill, D. Kim, Y. Jang, H. Kwon, D. Kim, G. Yeom,* Sungkyunkwan University (SKKU), Republic of Korea

For the selective isotropic etching of SiO_2 over Si_3N_4, due to the pattern sticking by a capillary action in nanoscale patterns, dry etch processing methods are widely investigated instead of wet etch processing especially for the next-generation semiconductor processing. Among various isotropic dry etching methods using plasmas, combinations of F-based gases and H-based reactive gases, such as NF_3/NH_3, OF_2/NH_3, CF_4/ NH_3, etc. have been investigated with downstream plasmas, remote plasmas, and so forth. In addition, these days, for the applications to various semiconductor devices, it is found that it is necessary to control the thickness of etched oxide thickness during the etching in addition to improving high selectivity over silicon nitride. In this study, selective isotropic cyclic dry etching of silicon oxide (SiO_2) was investigated using a three-step cyclic process composed of hydrogen fluoride (HF) adsorption by NF_3/H_2 remote plasma, reaction with NH_3 gas flow to form ammonium fluorosilicate ($(NH_4)_2SiF_6$), and desorption by heating. The variation of the ratio of NF_3:H_2 and adsorption time showed the variation of etch selectivity of SiO_2 over Si_3N_4. The characteristics of the cyclic remote plasma etching by NF_3/H_2 gas chemistry were analyzed by FT-IR and, the etch depth per cycle and etch profiles of SiO_2 were observed by an ellipsometer and FE-SEM.

PS-TuP-3 Identification of Critical Factors in Plasma Enhanced Atomic Layer Etching of Silicon Nitride through First-Principles-Based Simulations*, Erik Cheng,* *G. Hwang,* The University of Texas at Austin*; P. Ventzek, Z. Chen, S. Sridhar,* Tokyo Electron America

Viable plasma enhanced atomic layer etching (PEALE) of silicon nitride (SiN) by inert ion bombardment of a hydrofluorocarbon (HFC) treated surface has been demonstrated, but the details of the underlying mechanisms remain poorly understood. To this end, we have used molecular dynamics (MD) simulations based on the self-consistent-charge density-functional tight-binding (SCC-DFTB) theory to study the nonequilibrium chemistry and physics that can occur during PEALE of SiN with HFCs. From analyzing the results of thousands of such simulations, we have identified several potentially critical factors for the design of improved PEALE processes to be used in next-generation semiconductor manufacturing.

We first assessed the reactivity of surfaces, both with and without ion damage, and found it to be generally unreactive towards HFCs, suggesting that HFCs may primarily stay physisorbed, rather than chemisorbed, prior to ion bombardment.

Secondly, these physisorbed HFCs, upon ion bombardment, produce key decomposition fragments that may dictate the nature of the chemical modification that is achieved in the underlying film. This is seen when comparing CF4 and CH3F, the former primarily decomposing to CF2 and 2F while the latter decomposes to CH3 and F. As a result, CF4 results in greater amounts of F modification in the film, a tendency for C atoms forming higher order bonds with atoms in the film, and greater ion penetration depth.

Thirdly, we find that the nature of the film modification in PEALE is not only a function of NC and SiF bond formation, but that further SiC bond formation and defect generation in the film also have a major influence and may be important for volatilization of etch products. These etch products not only tend to contain F, but also H, C, and N, although to a lesser extent. However, at greater concentrations, we have demonstrated that F continues to be beneficial for volatilization, but that C and H can have adverse and neutral effects, respectively.

Our simulations have demonstrated the key roles of the complex dynamics induced by ion bombardment during PEALE, and we have highlighted key aspects identified from our analyses. Through understanding these key influences, development of improved PEALE processes could be greatly accelerated.

PS-TuP-6 Dry Etching of Co Thin Films Using High Density Plasma of Organic Gases

__Seon Jae Kim__, E. Lim, S. Park, S. Kim, C. Chung, Inha University, Republic of Korea

Copper interconnect, which has low resistivity, high electromigration resistance, and good mechanical properties, has replaced aluminum interconnect as the semiconductor devices are scaled down.However, as the semiconductor devices are increasingly scaled down, the metal interconnect line widths have been reduced to a level lower than 39 nm, which is the electron mean free path in the bulk state of copper. The scaling down in interconnect dimensions causes a resistivity size effect in which the resistivity of copper increases rapidly.Meanwhile, cobalt is a promising alternative for next-generation interconnect materials due to its lower resistivity at smaller dimensions (~10 nm), high melting point, and high compatibility with CMOS [1].

Despite the good properties of cobalt, dry etching of Co thin films have not been developed because Co has very low reactivity and its etch byproducts are nonvolatile. Therefore, it is necessary to develop an optimal etching gas and dry etching process for cobalt thin films.

In this study, dry etching of Co thin films patterned with TiN hard mask was carried out using inductively coupled plasma of organic gases. The etch rate, etch selectivity to hard mask, and the etch profile will be investigated using scanning electron microscopy and energy dispersive X-ray spectroscopy. The etch mechanism of cobalt thin films using organic gases will be examined using X-ray photoelectron spectroscopy.

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PS-TuP-8 Selective Etching of Silicon Nitride with Remote ClF_3/H_2 Plasma

__Seongjae Yu__, K. Kim, Y. Ji, J. Kang, G. Yeom, Sungkyunkwan University (SKKU), Republic of Korea

Highly selective etching of silicon nitride (SiN_x) over silicon oxide (SiO_y) is of great importance for oxide/nitride stacks in a 3D-NAND fabrication process. In this study, selective isotropic etching of SiN_x to SiO_y has been researched by adjusting a ClF_3/H_2 remote plasma in an inductively coupled plasma system. The etch rate of SiN_x over 80 nm/min and Selectivity (SiN_x over SiO_y) of ~130 was experimentally produced using ClF_3 remote plasma at a room temperature. Moreover, when H_2 was added to ClF_3, the selectivity increased to 200 while lowering the etch rate of both SiN_x and SiO_y as F radical is decreased in the plasma. The possible etch mechanism of SiN_x under Cl, F, H radicals was suggested based on the plasma and surface analyses. The etch characteristics of SiN_x and SiO_y according to the substrate temperature showed a higher activation energy of SiO_y compared with SiN_x under ClF_3 plasma.

PS-TuP-10 Layer-by-Layer Etching of Copper Thin Films Under Acetylacetone/O_2 Gas Mixture

__Seung Hyun Kim__, E. Lim, S. Park, C. Chung, Inha University, Republic of Korea

Previously, acetylacetone (acac) was employed at the gas cluster ion beam etching for copper films. They reported that the etch depth of copper using acac and O_2 gas mixture was deeper than that of copper using O_2 gas only, introducing the possibility of etching for copper films. However, they presented no etch profiles on copper films [1].

In this study, layer-by-layer etching of copper thin films was performed using acac/O_2 gas mixture and Ar plasma. Layer-by-layer etching involves two-step procedure, which contains the surface modification by the exposure of copper films to acac/O_2 gas and the elimination of the modified layers by the sputtering of Ar ions. The surface modification step was optimized by varying the flow-rate ratio of acac/O_2 gases and exposure time, which led to the oxidation of copper films and the formation of copper compounds. In addition, the elimination step also was developed by changing the dc-bias voltage to the substrate and sputtering time. The surface modification and elimination of the modified layers were verified by X-ray photoelectron spectroscopy and energy dispersive X-ray spectroscopy. The etch per cycle was obtained in the range of 0.7-3.0 nm/cycle, relying on the Ar sputtering at the fixed exposure condition. Layer-by-layer etching of copper films masked with SiO_2 presented good etch profiles without redepositions. Layer-by-layer etching of copper films using acac/O_2 gas mixtures can be one choice to demonstrate the fine pattern on copper films.

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PS-TuP-11 Enhancement of Plasma Uniformity Controlling Thermal Conductivity by Insulator Ring

__Jinuk Park__, J. Park, Sungkyunkwan University (SKKU), Republic of Korea

Regardless of the change over time, efforts to keep wafer edge's etch rate (ER) constant became an important area in etching technology as the size of wafer increased and the structure of the chip became more complicated. Therefore, semiconductor manufacturing facilities have developed to precisely etch the edge area. In this study, we developed a thermal interfacial material (TIM) with high thermal conductivity and changed the handling method of the TIM efficiently to improve used TIM Pad thermal conductivity.

TIM is implemented in the form of a pad having a heat dissipation component by adding thermal conductive fillers (AlN, Al2O3, Al) to a silicon-based resin. In this study, we will show you that feature of TIM pad depending on how to make TIM pad.

The characteristics of TIM pad is changed depend on how to deal with pad. In this paper, we will studied changed characteristic of TIM pad how long pad exposure to atmosphere and when does it make.

PS-TuP-12 Effect of $C_4H_2F_6$ Isomers on the Etch Characteristics of SiO_2

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As the device structure is scaling down in semiconductor devices, the requirements of higher selective etching process are increased. To meet the requirements, high aspect ratio contact (HARC) etching process is being developed in the direction to use more polymer forming fluorocarbon (PFC) and hydrofluorocarbon (HFC) gases. In addition, the PFC/HFC gases used for HARC etching for DRAM and 3D NAND devices such as C_4F_8, CHF_3 etc. have a long lifetime in the atmosphere when exhausted and have a high global warming potential (GWP) simultaneously. Therefore, to improve the etch selectivity for HARC etch processes and to replace the high GWP gases with low GWP HFC/PFC gases, various HFC/PFC gases are under investigation.

In this study, to understand the effect of the molecular structure of HFC gases on the etch characteristics of SiO_2 and its relationship to the GWP, $C_4H_2F_6$ isomer gases which are one kind of the high polymer forming HFC gases were used, and their dielectric etch characteristics and global warming effect depending on their molecular structure were investigated.

Even though the chemistry of the HFC isomers is the same, due to the different molecular structures, in addition to differences in the boiling points and the global warming potentials, the etch characteristics were different especially at a critical oxygen mixing percentage due to the differences in gas dissociation related to the specific chemical structure of $C_4H_2F_6$ isomer.

PS-TuP-13 Analysis on Ion Energy Distribution and Ion Mean Energy for All Radio-Frequencies and Pressures*, **Inho Seong**, S. Kim, Y. Lee, C. Cho, W. Jeong, Y. You, S. You,* Chungnam National University, Republic of Korea

As low-temperature plasmas have played a crucial role in modern semiconductor manufacturing, the understanding of ion energy distribution (IED) and ion mean energy at the electrode according to external control parameters is essential for satisfying a design rule. We studied IEDs and ion mean energy at the electrode in a wide range of frequency and pressure with an ion trajectory simulation coupled to Monte Carlo collision method. We observed a new tendency for the ion mean energy to increase and then decrease from low to high frequency in low pressure so that we analyzed ion trajectories for frequency and pressure regime. In addition, we found the frequency trend of the ion mean energy including the frequency region in which the ion mean energy is unchanged at a relatively high pressure and the frequency region shift of maximum ion mean energy. We are expected that these results show a different interpretation of the collision known as reducing the ion energy in the sheath.

PS-TuP-14 Moving Toward Antibacterial Wound Dressings: Modifying Commercially-available Materials Using Pulsed and Continuous-wave 1,8-cineole Plasma*, **Mia-Rose Kayaian**, M. Hawker,* California State University, Fresno

Hospital-acquired infections (HAIs) are one of the primary causes of mortality. According to Medicare data, HAIs are estimated to cost the United States anywhere from 28.1 to 96.8 billion dollars yearly. Most HAIs begin with bacterial attachment to the wound and, if left untreated, the infection site can become a chronic wound. For existing chronic wounds, oral and topical antibiotics are the clinical standards. This can become problematic because of the potential development of antibiotic resistance. Thus, incorporating a modification to the wound dressing that actively kills bacteria on contact without creating antibiotic resistance would be the best outcome for treating chronic wound infections. Plasma-enhanced chemical vapor deposition (PECVD) using 1,8-cineole (an active component of eucalyptus oil) as the plasma feed gas has been shown to actively kill bacteria on the surface of glass slides. Yet, 1,8-cineole-based PECVD strategies have not been extended to wound dressing materials.

The goal of the present study was to use 1,8-cineole PECVD to modify commercially-available wound dressing materials. By adjusting PECVD parameters, such as changing the applied power, it is possible to control the coating chemistry. However, no attempt has been made to compare pulsing vs. continuous-wave deposition. In other PECVD systems, pulsing has enabled the plasma precursor functional groups to be maintained within the coating. Because the functional groups give 1,8-cineole its antibacterial properties, we anticipated pulsing would enable the functional groups to be maintained upon PECVD. We hypothesized that wound dressing materials treated using pulsed plasma conditions would exhibit greater antibacterial properties compared to those treated with continuous conditions because pulsing allows for the functional groups to be maintained. Water contact angle goniometry was used to evaluate changes in surface wettability before and after plasma treatment. Additionally, x-ray photoelectron spectroscopy was used to quantify the elemental composition of plasma-treated and control surfaces. Zone of inhibition testing was performed to evaluate antibacterial properties against both gram-positive and gram-negative bacteria. Overall, previously established 1,8-cineole PECVD strategies were extended to wound dressing materials. This work represents progress towards addressing the need to directly target chronic wound infectious sites.

PS-TuP-15 To What Extent Do Nitrogen and Water Vapor Plasma Treated Silk Films Exhibit Hydrophobic Recovery?*, **Ashley Keobounnam**, C. Lenert-Mondou, M. Hawker,* California State University, Fresno

Silk fibroin (silk) is a naturally-derived polymer from the bombyx mori cocoon. Silk has great potential applications for biomedical use due to its mechanical strength, non-immunogenic properties, and ability to biodegrade. However, the hydrophobic nature of silk can cause challenges with cell adhesion in vivo. Therefore, modification must be performed to improve the surface hydrophilicity. Low-temperature plasma (LTP) modification is a well-established method for polymer modification and has the benefits of being a solvent-free process. Nitrogen and water vapor LTP are both well-documented as strategies to enhance polar functional groups on a polymer's surface. However, LTP-modified polymers have been documented to experience hydrophobic recovery. During hydrophobic recovery, the modified polymer chains rearrange from a higher to lower surface energy state, negating the effects of LTP modification. Notably, the hydrophobic recovery of LTP-modified silk has not been previously studied.

The goal of this study was to systematically evaluate the hydrophobic recovery of nitrogen and water vapor LTP treated silk films. Silk films were dropcast on glass slides and were LTP-modified using optimized plasma parameters (applied power, pressure, and treatment time). Interactions between silk films and water were evaluated with water contact angle goniometry. Initial results showed that untreated silk films exhibited water contact angles of 69 +/- 1°. After nitrogen and water vapor LTP treatments, the films showed water contact angles of 35 +/- 1° and 25 +/- 2°, respectively, demonstrating a significant decrease in hydrophobicity. Films were then aged under ambient conditions up to 6 weeks and analyzed at specific time points (0 days, 7 days, 21 days, and 42 days). Both the nitrogen and water vapor plasma-modifed silk film water contact angles remained relatively stable throughout the 42 day aging period, suggesting that minimal hydrophobic recovery occurred.

PS-TuP-16 Ion Energy Control Independent with Ion Density Using a Passive Antenna in an Inductively Coupled Plasma Source*, **Minsu Choi**, S. Kim, I. Seong, C. Cho, Y. Lee, W. Jeong, Y. You, B. Choi, S. You,* Chungnam National University, Republic of Korea

As elaborate etching such as atomic layer etching becomes a challenge in modern semiconductor and display processes, The precise independent control of ion energy and density for accurate etching has attracted tremendous interest. While previous techniques have focused on a variant of the electrical system called active control, this study proposes a method via a passive antenna without active control.

The proposed technique controls electromotive force induced by the inductive coupling between the discharge antenna and the passive antenna, which varies plasma potential and finally ion energy. To verify the proposed technique, ion energy distribution (IED) and plasma potential were measured by an ion energy analyzer and emissive probe, respectively, and the electromotive force was controlled by adjusting the distance between those antennae.

The experiment result shows the increase of plasma potential and ion energy with constant ion density as the antennae distance decreases. This result means that ion energy can be controlled independently of ion density by using the passive antenna.

This study demonstrated the ion energy control technique independent of its density with a passive control and would be applicable for future semiconductor processing.

PS-TuP-17 The Impact of Si_3N_4 Ultra-thin Layer on InN Growth on Si(111) by RF-MOMBE*, **Wei-Chun Chen**,* Taiwan Instrument Research Institute, National Applied Research Laboratories, Taiwan*; S. Chen, C. Cheng,* Department of Mechatronic Engineering, National Taiwan Normal University, Taiwan

Si_3N_4 ultra-thin layer were grown on Si(111) surface by RF N_2 plasma exposing with various N_2 flow rate and nitriding time. After the Si_3N_4 thin films were as a buffer layer for the InN crystals growth. We discussed the effect of InN/Si_3N_4 ultra-thin film on the optical, chemical, structural properties. The results indicated that stoichiometric Si3N4 ultra-thin film was obtained at nitridation time nearly to 1hr with RF power of 300 W and N2 flow ratio at 1.2 sccm. Also, AFM image exhibited that the Ra roughness of Si_3N_4 is 0.39 nm. On the other hand, XRD phi-scan results shows that the InN crystals epitaxy growth with Si(111) substrate. Also, the InN crystals were detected single crystals growth with grown the crystal along the <0001> direction (c-axis). Cross-sectional SEM images show the nanocolumns with surface texturing of pyramid-like.

PS-TuP-18 Machine Learning Based Surrogate Models for Capacitively Coupled Plasmas*, L. Yan,* Applied Materials, Inc. (Currently with University of Pennsylvania)*; **Abhishek Verma**, S. Ganta, K. Bera,* Applied Materials, Inc.

Plasma simulations are instrumental in understanding fundamental plasma behavior in plasma reactors used for etching and deposition processes in semiconductor manufacturing. However, these models are often slow to execute for large scale problems, limiting their applicability in design optimization and process control. To overcome these limitations, we recently developed a machine learning framework based on deep learning methods (LSTM and CNN-AE) to construct surrogate models at reduced computational cost while maintaining accuracy. Radio frequency (RF) plasma simulations have been performed using in-house code for Ar discharge. RF potential amplitude and phase differences at several harmonics are generated utilizing design of experiments and used to drive the plasma at different pressures. We used plasma characteristics from simulations, such as generated current *I(t)*, plasma density *n(x,t)* with respect of voltage *V(t)* to train and test on datasets under different conditions (e.g., pressure). We obtained the optimal model through experiments with comprehensive search of different hyper-parameters and model architectures. In time series prediction of current *I(t)*, we used *n* past values of two voltage channels and their time derivatives as inputs to a LSTM based model and showed that averaging prediction results given by models trained on different past values could lead to further accurate and smooth results. Furthermore, our model performs satisfactorily for the prediction of current *I(t)* even at a different operating frequency from the one that the model was trained on. Finally, we demonstrate optimal compression of spatial variables such as plasma density *n(x,t)* using CNN based autoencoder.

PS-TuP-19 Chemistry Reduction in Fluid Plasma Simulations*, **Ramanish Singh**,* Applied Materials Inc. (Currently with University of Minnesota)*; S. Ganta, A. Verma, K. Bera,* Applied Materials, Inc.

Plasma modeling for semiconductor process applications can help in gaining insights into various mechanisms occurring during the processes, playing a vital role in optimizing these processes. However, as the complexity of the plasma chemistry increases (large number of species and reactions), these models become prohibitively expensive in terms of computational cost. Such chemistries can be reduced by removing unimportant species and reactions to reduce computational cost with minimal loss in accuracy. To this end, we developed a general Python-based chemistry reduction methodology that utilizes fluid plasma simulation results for identifying important chemical pathways based on production rates of relevant species thereby generating multiple sets of reduced chemistries. We use PumpKin[1], an open-source C++-based software for identifying important chemical reaction pathways given a chemistry with reaction rates and stoichiometric data from a plasma simulation. Once the multiple reduced chemistries are obtained, the chemistry reduction model assesses their accuracy, helping with the selection of the most suitable reduced chemistry for a particular application. We also developed an alternate technique for chemistry reduction involving direct species removal, wherein species and their associated reactions are removed based on their steady-state time-averaged densities relative to that of other similar species in the chemistry. We tested the two methodologies for chemistries belonging to different plasma processes such as plasma-enhanced chemical vapor deposition (PECVD), plasma-enhanced atomic layer deposition (PEALD), and conductor etch. We observe that chemistry reduction model based on species production rates removes a high number of unwanted reactions (~40-50%) and around 5-6 % of unimportant species while maintaining an error of less than 3% between the full chemistry and the reduced chemistry. In the direct species removal algorithm, although the number of species removed is marginally higher for a given error threshold, very few reactions get eliminated. We also investigated the effect of running both the algorithms in the two possible two-step sequences. The model based on species production rates followed by direct species removal results in a chemistry reduction with a good balance between model accuracy and computational cost optimization. However, the results can vary according to the chemistry used in the semiconductor process application.

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Surface Science Division
Room Ballroom A - Session SS-TuP
Surface Science Poster Session

SS-TuP-1 Monolayer Functionalization of Semiconductor and Metal Oxide Surfaces with Boron-Containing Precursors*, **Dhamelyz Silva Quinones**, C. Byron, A. Teplyakov,* University of Delaware

The monolayer functionalization reactions of Si (100) single crystal with boron-containing compounds, including boron trichloride, boric acid, and 4-fluorophenylboronic acid were studied in order to understand the interactions of these molecules with hydrogen and chlorine terminated-Si (100) for designing possible silicon doping processes. This study was compared with the surface modification of TiO_2 and Al_2O_3 nanoparticles with 4-fluorophenylboronic acid in solution in order to understand the attachment chemistry and to develop spectroscopic labels for surface characterization.

The modification chemistry was followed by X-ray photoelectron spectroscopy (XPS), solid-state NMR (ss-NMR), and infrared spectroscopy to determine the binding modes of the attached compound. Density functional theory was utilized to supplement the analysis, interpret the results of spectroscopic measurements, and to interrogate the surface stability of possible surface species.

The results obtained in these studies confirm the attachment of the boron trichloride, boric acid, and 4-fluorophenylboronic acid showing selectivity for the Cl-terminated Si (100) surface compared to H-terminated Si (100).

The attachment chemistry of 4-fluorophenylboronic acid on the TiO_2 and Al_2O_3 nanoparticles was confirmed with a high coverage and the type of attachment on each metal oxide surface is described.

This work provides fundamental understanding and a new pathway to obtain functionalized flat and nanoparticulate surfaces with boron-containing molecules. In the case of flat surfaces, these reactions can be used for selective-area monolayer doping or as a deposition resist. For oxide nanomaterials, the same approach can be used for spectroscopic labeling or for further functionalization.

SS-TuP-2 Detection of Chemically-induced Hot Electron Flux Amplified by Plasmonic Effect on Pt/Ag/TiO_2 Nanodiodes*, **Mincheol Kang**, B. Jeon, J. Park,* Korea Advanced Institute of Science and Technology (KAIST) & Institute for Basic Science (IBS), Republic of Korea

Concern about the energy resource crisis has encouraged study of the conversion and utilization of solar energy to improve catalytic efficiency, and the design of the surface plasmon-based photocatalyst is attracting particular attention as a competitive catalyst system. In this work, catalytic devices based on Schottky nanodiodes (Pt/Ag/TiO_2) were fabricated for antenna-reactor plasmonic photocatalysis; hot electrons generated during the chemical reaction can be directly detected through the diodes. In this system, the surface temperature was measured using thermovision to distinguish contributions of the plasmonic effect and the photothermal heating effect. When the light of the particular wavelength region is incident on the diodes, the flow of reaction-induced hot electrons (chemicurrent) and the catalytic activity (turnover frequency) are amplified by the plasmonic effect. Plasmonic photocatalytic performance can be controlled with light wavelengths, light intensity, surface temperature, and structures of nanodiodes. Also, the plasmonic effect is exhibited visually, using the finite difference time domain simulations. These results elucidate the hot electron flow on antenna-reactor photocatalysis and offer improved strategies for efficient catalytic devices.

SS-TuP-3 Boosting Hot Electron Generation and Catalytic Performance by Engineering Metal-Oxide Interfaces*, **Kyoungjae Song**, J. Park,* Korea Advanced Institute of Science and Technology (KAIST) & Institute for Basic Science (IBS), Republic of Korea

The interface between catalytic metal and oxide support is an important factor that affects reaction performance. However, metal-oxide and oxide-oxide interface studies have been limited, because of the complex structure of metal-oxide-oxide interface. To investigate the influence of the complex interfaces on both catalytic performance and hot electron flux, we used an inverse oxide-metal Schottky diode from CeO_2/ $Co\text{-}_3O_4$ nanocubes (NCs) on Pt film, which measures hot electron flux and reaction rate under an exothermic methanol oxidation reaction. Turnover frequency (TOF), partial oxidation selectivity, and hot electron flux were obtained on CeO_2/ $Co\text{-}_3O_4$ NCs on Pt film; TOF was higher by a factor of 2,selectivity to methyl formate was higher by a factor of 1.5, and chemicurrent yield was higher by a factor of 7 compared to Co_3O_4 NCs on Pt film. Furthermore, the Co_3O_4

NCs half covered with CeO_2 showed higher values of both TOF and selectivity to methyl formate than CeO_2 NCs and Co_3O_4 NCs fully covered with CeO_2, indicating that the Co_3O_4/CeO_2 interface also affects the catalytic reaction. From ex situ XPS analysis, CeO_2-Co-$_3O_4$ on Pt film showed the highest proportion of Ce^{3+} ions compared to both CeO_2 NCs and Co_3O_4 NCs fully covered with CeO_2 nanoparticles. The result indicate that CeO_2 can not only prevent the reduction of Co_3O_4 by supplying oxygen, but also boosts the methanol oxidation reaction by supplying oxygen to Pt film, leading to enhanced hot electron flux.

SS-TuP-4 Effect of Water Vapor on Oxidation Process of Cu(111) Surface and Sublayer; Ambient Pressure STM and XPS Studies*, **Youngjae Kim**, D. Kim, Y. Kim,* Korea Advanced Institute of Science and Technology (KAIST) & Institute for Basic Science (IBS), Republic of Korea*; Y. Jeong,* Institute for Basic Science (IBS), Republic of Korea*; B. Jeong,* Korea Basic Science Institute (KBSI), Republic of Korea*; J. Park,* Korea Advanced Institute of Science and Technology (KAIST) & Institute for Basic Science (IBS), Republic of Korea

Copper-based materials are used for heterogeneous catalytic reactions, including CO oxidation, low-temperature water gas shift reactions, and CO_2 hydrogenation. These applications could benefit from a better understanding of the transitions between copper-based oxidation states, metallic Cu, Cu_2O, and CuO. In this work, we directly observed different oxidation processes on a Cu(111) single crystal, using ambient pressure scanning tunneling microscopy (AP-STM) and X-ray photoelectron spectroscopy (AP-XPS). The Cu(111) surface started to be oxidized at 0.01 Torr of pure O_2 under dry oxidation conditions. Time-lapse AP-STM and AP-XPS results showed that dry oxidation started at the step-edges in the form of adsorbed oxygen atoms, $O_{(ad)}$, and progressed to the terrace in the Cu_2O phase. In addition, independent oxidations on the metallic Cu(111) terrace provided a more collapsed Cu_2O/Cu(111) surface structure. Under H_2O/O_2 mixed gas conditions, the humid oxidation of the Cu(111) surface occurred at 0.02 Torr. Time-lapse AP-STM images demonstrated that the oxidation also proceeded from the step-edges to the terrace, but there were no independent oxidations on the terrace, leading to fewer defect sites on the Cu_2O/Cu(111) surface. Time-lapse AP-XPS results showed that the appearances of $O_{(ad)}$ and Cu_2O peaks were similar to dry oxidation. Hydroxides were observed after the surface was completely saturated by the Cu_2O phase. Furthermore, by analyzing the relative intensity and peak area of XP spectra, we found that the depth of Cu_2O differed dramatically in the dry and humid oxidation processes. The Cu_2O thickness of the dry oxidation was greater than that of the humid oxidation under all similar pressures. Water molecules from the humid oxidation caused a different oxidation mechanism from the dry oxidation, with a different degree of oxidation.Specifically, the water vapor molecules inhibited sublayer oxidations, inducing less coverage of the step-edges on the Cu(111) surface than under the dry oxidation conditions.

SS-TuP-5 Phase-Dependence on the Friction of Exfoliated MoX_2 (X:S, Te) Layers*, **Dooho Lee**,* Korea Advanced Institute of Science and Technology (KAIST) & Institute for Basic Science (IBS), Republic of Korea*; H. Jeong,* Korea Advanced Institute of Science and Technology, Republic of Korea*; H. Lee,* Korea Advanced Institute of Science and Technology (KAIST) & Institute for Basic Science (IBS), Republic of Korea*; Y. Kim,* Korea Advanced Institute of Science and Technology, Republic of Korea*; J. Park,* Korea Advanced Institute of Science and Technology (KAIST) & Institute for Basic Science (IBS), Republic of Korea

Transition metal dichalcogenides (TMDs) 2-dimensional (2D) material is widely studied for its semiconducting nature, which makes it potentially suitable for applications in thin-film transistors.[1] Among TMDs, the molybdenum disulfide (MoS_2) monolayer is an atomically thin semiconductor with a bandgap of 1.8 eV. MoS_2 is also getting attention as an anode for Li-ion batteries, because of its Li intercalation mechanism. Electron donations from Li induce a MoS_2 phase transition from the stable semiconducting 2H phase to the metallic 1T phase. While MoS_2 chemically exfoliated with Li showed friction at a similar level with mica, mechanically exfoliated MoS_2 exhibits significantly lower friction than mica.[2]

We turned mechanically exfoliated 2H-MoS_2 into 1T-MoS_2 by a lithiation process and measured atomic-scale tribological and electrical properties of MoS_2, including friction, with atomic force microscopy (AFM). We report that the friction of MoS_2 increased significantly with the phase transition of 2H to 1T. The friction proportion of 2H-MoS_2 and 1T-MoS_2 is 0.12:1.07, with normalization to the value of mica. We also measured the friction of molybdenum ditelluride ($MoTe_2$), of which the pure 1T phase is commercially available, since it shows a stable 1T phase as well as a 2H phase. The friction proportion of exfoliated 1T-$MoTe_2$ and 2H-$MoTe_2$ is 0.18:1.09, normalized with the friction of mica. With density functional theory (DFT) calculation, we attribute the higher friction of 1T-MoX_2 to the increased overlap of phonon density of states (DOS) with mica substrate, as well as the higher energy barrier in the potential energy surface of 1T-MoX_2. The study suggests the intriguing possibility of tuning friction by a phase transition of 2D materials.

References

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SS-TuP-6 Electron Dynamics at a Confined $Cu_{2-x}O$/Cu Interface*, **J. Trey Diulus**, J. Beckord, Z. Novotny, N. Comini, M. Hengsberger, J. Osterwalder,* University of Zurich, Switzerland

Cuprous oxide (Cu_2O) is a promising photocathode material for the hydrogen evolution reaction (HER) due to its bandgap in the visible spectrum, relative abundance, and low cost. However, Cu_2O is unstable in aqueous solutions. To increase the corrosion resistance, a chemically stable capping layer, such as hexagonal boron nitride (*h*-BN), can be deposited on the Cu_2O surface. While the growth of *h*–BN on top of non-metallic oxides by chemical vapor deposition is difficult, one approach is to oxidize a Cu metal substrate underneath an *h*-BN monolayer via O_2 intercalation. This preparation method was implemented by exposing a Cu(111) single crystal with an h-BN monolayer to partial pressures of O_2 up to the millibar range at temperatures up to 200 °C. The atomic structure was unraveled with a combination of surface science techniques at the Swiss Light Source. The h-BN layer remains intact and the $Cu_{2-x}O$ oxide film has a thickness of a few atomic layers (3-4 Å) displaying structural motifs typical of the Cu_2O(111) surface, comprising a chemisorbed O layer and a $Cu_{2-x}O$-like trilayer positioned in between the h-BN and the substrate. A well-ordered *h*–BN/$Cu_{2-x}O$/Cu(111) sample was prepared for characterizing the electronic structure and electron dynamics with ultraviolet and pump-probe photoemission spectroscopy. Angle-resolved photoelectron spectroscopy (ARPES) after oxidation shows the sharp σ and π bands of an intact *h*-BN monolayer and another narrow state 1.2 eV below the Fermi level, attributed to the valence band of Cu_2O that is shifted downwards due to the contact to a metallic copper substrate. Time-resolved two-photon photoemission (tr-2PPE) spectra show a short-lived state at 1.0 eV and a long-lived state at 0.1 eV above the Fermi level. The state at about 1 eV has a strong parabolic dispersion matching the conduction band of Cu_2O, whereas the low energy state has no dispersion, pointing towards a localized defect state of the $Cu_{2-x}O$ layer. Such defect states were also observed on the reconstructed bulk Cu_2O(111) surface and were attributed to charged oxygen vacancy states with very high capture coefficients for trapping conduction electrons. The visible conduction band is promising, but the trapping is detrimental to the function as efficient photocatalyst. To render this system into a viable photocathode, the oxide film should be grown to a thickness adapted to the light absorption length of about 30 nm, and the defect concentration should be further reduced.

SS-TuP-7 Understanding Interfaces to Develop Advanced Materials for Industrial Applications*, **Pierluigi Bilotto Bilotto**, M. Ostermann, D. Miano,* Centre for Electrochemistry and Surface Technology (CEST GmbH), Austria*; M. Valtiner,* Centre for Electrochemistry and Surface Technology (CEST Gmbh), Vienna University of Technology (TUW), Austria

Industries eager for innovative solutions to strike against the climate crisis. For instance, that translates into developing innovative composites material expressing multifunctionalities, reduce the energy produced because of wearing via green solid lubricant, or for instance optimizing yield and efficiency of industrial processes.

The poster will summarize the projects and results obtained at the Centre for Electrochemistry and Surface Technology (CEST, Austria) in the *material and interfaces* research areas for application in aeronautical, aviation and semiconductor industries. Specifically, we propose a clean and upscalable process for the production of graphene oxide, [1] which will be used for advanced coatings expressing de-icing, lightning strike protection and corrosion functionalities. Moreover, for the *interface* area we will show our strategies to elucidate the tribological mechanisms of MXenes based solid lubricant, and the utilization of nanobubbles to optimize wafer cleaning processes.

(1) Ostermann M. *et al* – (submitted in May 2022)

SS-TuP-8 Investigation of CO Oxidation on Rh(111) with IRRAS, ***Faith Lewis**, D. Killelea,* Loyola University Chicago

Fourier-transform Infrared (FTIR) spectroscopy is widely applied to identify small molecules adsorbed to metal surfaces. Here, FTIR was coupled to an ultra-high vacuum (UHV) system where the sample environment was carefully controlled to eliminate interference from atmospheric species. IR reflection measurements from a metal surface were performed under UHV conditions and the catalytic oxidation of carbon monoxide (CO) to carbon dioxide (CO2) over Rh(111) was investigated. This reaction was used as a probe reaction to determine the relative reactivity of various oxidic species. We determined the binding sites on different oxygenaceous phase and determined their chemical significance towards heterogeneously catalyzed oxidation of CO. This provided atomic level information regarding oxidation reactions, and advanced our understanding of the different surface phases relevant to many Rh catalyzed processes.

SS-TuP-9 Modifications of Surface Optoelectronics in ZnO Nano- and Microcrystals Following Exposure to *Staphylococcus Aureus* and Bacterial Growth Media, ***Dustin Johnson,*** Texas Christian University*; J. Reeks,* INSTITUTE OF LOW TEMPERATURE AND STRUCTURE RESEARCH - POLISH ACADEMY OF SCIENCES, Poland*; A. Caron,* Texas Christian University*; I. Tzoka,* University of Texas at Arlington*; O. Castillo, K. Nguyen,* Paschal High School*; M. Hattarki,* Rice University*; S. McGillivray, Y. Strzhemechny,* Texas Christian University

A combination of useful optoelectronic properties and high biocompatibility rendered ZnO a versatile material with budding applications at the nano- and microscale, among which are pharmaceutics, bioengineering and medical diagnostics, specifically employing ZnO as an antibacterial agent. With bacterial growth inhibition observed for both gram-positive and gram-negative bacteria as well as antibiotic strains, the antimicrobial action of ZnO is both promising and well documented. Yet application is significantly hindered due to uncertainty regarding fundamental mechanisms underlying such properties. Presently, discussion centers on several proposed mechanisms, such as generation of various reactive oxygen species, Zn ion release and surface-surface interactions between the bacterial cell wall and free crystalline surface. Here we investigate surface and near-surface modifications of optoelectronic properties in ZnO microcrystals following exposure to bacterial environments to elucidate those specific mechanisms. Microscale ZnO crystals are well-suited to serve as a platform to investigate the role played by crystalline surfaces as they exhibit comparable antibacterial action to nanoscale forms while minimizing effects of internalization. A bottom-up hydrothermal growth method allows for controlled synthesis of high-quality ZnO microcrystals with tunable morphology and controllable relative abundance of polar vs. non-polar surfaces. The quality of crystalline lattice and free surface as well as the predominant morphology of these samples are confirmed by FE-SEM, EDXS, and surface photovoltage (SPV) studies. The antimicrobial efficacy of these particles is characterized by minimum inhibitory concentration assays, utilizing wild type *s. aureus* in Mueller Hinton broth media. A series of optoelectronic experiments including temperature-dependent PL spectroscopy as well as spectroscopic and transient SPV are performed to probe changes occurring at ZnO surfaces during such assays. These comparative studies reveal that antibacterial action of ZnO microparticles is primarily rooted in interactions between crystalline surfaces and extracellular material of the bacteria. This is supported by observed degradation of the crystal surface and significant spectral changes due to surface interactions with bacteria and growth media. We show that interaction with *s. aureus* results in considerable change to the excitonic structure of the ZnO microcrystals. We also demonstrate dependence of such interactions on growth media, specifically those containing aqueous phosphates, finding not only changes in bactericidal efficacy but also the nature of these interactions.

SS-TuP-10 A Potential Model for Investigating the Edge Properties of FeO by Taking Advantage of Different Metal Affinities, ***Dairong Liu**, L. Li, S. Mahapatra, N. Jiang,* University of Illinois - Chicago

As a series of catalysts with wide catalysis applications and high economic efficiency, iron oxide has caught extensive attraction in the past several decades. During the various types of iron oxide, the FeO, well known as Ferrous oxide, has been proved to have high catalysis reactivities in catalysis reaction, e.g. CO catalysis oxidation. To obtain a throughout understanding of the catalysis mechanism, it is vital to investigate the surface and edge properties of FeO. In the past decade, various techniques have been applied the reach the surface properties of FeO, the researchers found that the edge of FeO plays an important role in the initial CO oxidation. However, due to the limit of the characteristic technique, the specific edge properties of FeO are still under debate. Here, we established a model, to selectively expose the distinguished type of edges on FeO. By taking advantage of the different metal affinities of the O-edge and Fe-edge in FeO, the Pd and Pt are introduced and found to selectively block the distinguished edge. The blocked edges are expected to be excluded from the catalysis reaction, which means that in the reaction, only the unblocked type of edge will be involved. By further comparison of the different performances of Fe-edge and O-edge selective exposed samples, the roles of different types of edge in the catalysis reaction can be studied, which can give an insight into the edge properties of the FeO and contribute to the design of high-efficiency FeO catalyst.

SS-TuP-11 Effects of Thermal Atomic Layer Etching on the Magnetic Properties of CoFeB, ***Marissa Pina**, M. Konh, Y. Wang, J. Xiao, A. Teplyakov,* University of Delaware

Atomic layer etching (ALE) is emerging as a major approach to control feature size of modern devices at the atomic scale. Thermal approaches are especially important for expanding the capabilities into the 3rd dimension and approaching more-than-Moore technology. However, for complex materials that are used in spintronics and magnonics, developing thermal ALE methods is difficult because the materials often contain several elements, some of the elements have not been investigated for ALE, little control over the surface properties of the resulting films is established, and their effect on the physical properties of the device (such as magnetic properties) has not been investigated. This work will interrogate the chemistry of thermal ALE of CoFeB alloys used in the magnetic tunnel junction and present an investigation of the effect of this chemistry on the magnetic properties of thin films. The effect of a half-cycle of chlorination and a full cycle of exposure to chlorine and acetyl acetone will be compared for films of comparable thickness produced by multiple ALE cycles and by ion milling. The effect of chemistry and surface smoothing will be evaluated based on a comparison of surface characterization by atomic force microscopy and XPS with the outcomes of ferromagnetic resonance measurements. Further pathways for controlling the effects of ALE on the physical properties of thin films prepared from different materials will be proposed.

SS-TuP-12 The Diamond (111) Surface Reconstruction and Epitaxial Graphene Interface, ***Benjamen Reed,*** National Physical Laboratory, UK*; M. Bathen,* ETH Zurich, Switzerland*; J. Ash,* Aberystwyth University, UK*; C. Meara,* Newcastle University, UK*; A. Zakharov,* Max IV Laboratory, Sweden*; J. Goss,* Newcastle University, UK*; J. Wells,* University of Oslo, Norway*; D. Evans,* Aberystwyth University, UK*; S. Cooil,* University of Oslo, Norway

There is rejuvenated interest in (111)-orientated diamond as a state-of-the-art electronic material, especially for quantum information and sensing applications, and its nanoscale properties for the production of diamond-graphene interfaces. However fundamental studies of the diamond (111) surface remain incomplete and there is an unresolved controversy surrounding the electronic nature of the C(111)-(2×1) surface. Density functional theory (DFT) calculations predict symmetrically π-bonded surface chains that exhibit a metallic surface state that intersects the Fermi level (E_F),[1,2] but experimental angle-resolved photoemission spectroscopy (ARPES) studies have shown a semiconducting surface ($\Delta E = 0.5$ eV) that corresponds to a dimerized π-bonded surface chain model.[3,4]

Our combined ARPES and DFT results show that the C(111)-(2×1) surface is metallic as it has electronic states that intersect E_F. This is in strong agreement with a symmetrically π-bonded chain model and should contribute to resolving the controversies that exist in the literature surrounding the electronic nature of this surface. Above 1000°C in vacuo, the reconstructed surface atoms are liberated into a free-standing monolayer of epitaxial graphene which exists above a newly formed C(111)-(2×1) surface and appears to have little substrate interaction as the Dirac-point is observed at E_F. We also demonstrate that is possible to hydrogen terminate the underlying diamond surface by means of plasma processing without removing the graphene layer, forming a graphene-semiconductor interface.[5]

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SS-TuP-13 The Nature of Electrical Double Layer Near Graphene and Anatase*, **Xiao Zhao**, S. Yang, M. Salmeron,* LBNL

Structure and profiles of electrical double layer (EDL) govern many electrochemical reactions. Fundamental knowledge of EDL is based on simplified Gouy-Chapman and Stern model, in which solvation and specific interactions of the electrolyte ions with the electrode are neglected. Here we present our recent progress determining the EDL structure near substrate-free graphene and near thin anatase films using Raman, Sum Frequency Vibrational Spectroscopy (SFVS), Kelvin Probe Force Microscopy (KPFM) and Near Edge X-ray Absorption Fine Spectroscopy (NEXAFS). Near suspended graphene SO_4^{2-} anions were found to preferentially accumulate near the interface at open circuit potential (OCP), creating an electrical field that orients water molecules below the interface while no such increase was observed with Cl^-. The degree of orientation of the water molecules as well as the electrical double layer strength increased further when positive voltages are applied. Negative voltages on the other hand produce smaller changes in the intensity of the H-bonded water peaks, but affect the intensity and frequency of the dangling O-H bond peaks. Near anatase ice-like water layer has been observed using SFVS and NEXAFS, and different segregation behavior has been observed for Na^+ and Cl^- under both OCP and applied bias. Our findings demonstrate the effect of solvation n and electrode-ion interactions on EDL structure and call for theoretical insight in this direction.

SS-TuP-14 Reactions of Tetrakis(Dimethylamido)Titanium on Halogenated, Hydrogenated, and Oxidized Silicon Monolayer Resists for Atomic Layer Deposition*, **Tyler Parke**, D. Silva-Quinones, A. Teplyakov,* University of Delaware

In atomic layer deposition (ALD) of TiO_2 with titanium tetrachloride ($TiCl_4$) and water, silicon (100) substrates with atomic chlorine (Cl-Si) or hydrogen (H-Si) terminations have previously been shown to be non-growth surfaces, resisting adsorption of and reaction with $TiCl_4$, as opposed to reactive oxidized silicon (HO-Si) growth surfaces, upon which $TiCl_4$ readily deposits. However, Cl-Si(100) degrades and loses selectivity rapidly under ALD conditions, leading to $TiCl_4$ nucleation on oxidized surface sites. In contrast, tetrakis(dimethylamido)titanium (TDMAT) follows a different reaction pathway on Si(100) surfaces, implying a difference in TDMAT's surface selectivity on silicon terminated with chlorine or perhaps other halogens, as well as a difference in the mechanism and extent of the selectivity loss. Here, the reactivity of TDMAT was studied under ALD conditions with oxidized, halogenated, and hydrogenated Si(100) surfaces. TiO_2 deposition was monitored on each surface using *ex situ* X-ray photoelectron spectroscopy (XPS). The initial nucleation behavior in the first few ALD cycles was compared between each surface using atomic force microscopy (AFM). Details of the bonding of TDMAT to the surface were elucidated using spectroscopic data in conjunction with density functional theory (DFT) observables on models of local surface geometry to propose surface reaction pathways.

SS-TuP-15 A 2D Bismuth-induced Honeycomb Surface Structure on GaAs(111)*, **Yi Liu**, S. Benter,* Lund University, Sweden*; C. Ong, R. Maciel, O. Eriksson,* Uppsala University, Sweden*; A. Mikkelsen, R. Timm,* Lund University, Sweden

Bi-containing III-V semiconductors are of significant interest due to their superior charge carrier mobility, tunable direct band gap, large spin-orbit splitting, and predicted non-trivial topological behavior. This is relevant for realizing quantum information technology due to a large flexibility in material combinations and a potential for room-temperature operation. However, the realization of ordered, crystalline alloys with high Bi content remains a challenge. Epitaxial growth of III-V films only allowed dilute compounds with very low Bi atom incorporation, while surface evaporation has typically demonstrated Bi metallic films on top of the semiconductor surfaces. Instead, formation of ordered 2D semiconducting III-V:Bi films remains a desired alternative.

Here, we present the successful Bi incorporation into a clean GaAs(111)B surface, based on Bi deposition under optimized growth conditions. Atomically resolved low-temperature scanning tunneling microscopy and spectroscopy (LT-STM/S) shows a well-ordered large-scale honeycomb structure, consisting of Bi atoms in a $\sqrt{3}\times\sqrt{3}$ 30° reconstruction on GaAs(111). An almost defect-free, large-scale honeycomb structure is obtained after short anneal. X-ray photoelectron spectroscopy proves the successful incorporation of Bi atoms in the GaAs surface and shows that the Bi atoms of the honeycomb structure only bond to the underlying As atoms. This is supported by density functional theory calculations which confirm the honeycomb structure, including a preferential formation of Bi-As bonds, and predict Bi-induced electronic bands within the GaAs band gap that open up a gap of non-trivial topological nature. STS results support the existence of Bi-induced states within the GaAs band gap.

The ordered Bi-induced 2D layer with a high Bi content of up to 67% surface coverage, covalently bonded to the GaAs substrate, and indications for non-trivial topological behavior is a great step towards realizing III-V semiconductor heterostructures with high Bi content that make use of the large spin-orbit coupling of Bi for enabling novel electronic properties. Furthermore, this result is a successful example for Bi-introduced low-dimensional structures with unique electronic states in III-V semiconductor systems.

SS-TuP-16 Hydrochloride Production from Dichlorosilane Decomposition and Its Impact on Atomic Layer Deposition of Silicon Nitride*, **Tsung-Hsuan Yang**, E. Cheng, G. Hwang, S. Johnson, J. Ekerdt,* University of Texas at Austin*; P. Ventzek, T. Iwao, J. Zhao,* Tokyo Electron America Inc.,*; K. Ishibashi,* Tokyo Electron Ltd., Japan

Plasma-enhanced atomic layer deposition (PEALD) has been demonstrated to be a promising technique for the controlled growth of silicon nitride (SiN) thin films. The advantages of PEALD include excellent conformality, precise thickness control, and high quality at relatively low temperatures. In this talk, we will present molecular mechanisms underlying the PEALD of SiN thin films using dichlorosilane (DCS) as the Si source and N_2/NH_3 plasma as the N source. The adsorption and decomposition of DCS have been found to be sensitive to the surface functional groups; especially, the presence of primary amines plays a critical role in the silicon deposition half cycle. According to our recent studies, the by-products of DCS decomposition, H^+/Cl^- pairs, may have a significant effect on the film quality and deposition temperature. First-principles calculations predict that H^+/Cl^- pairs are strongly bound to the H-terminated N-rich surface by forming –NH_3^+/Cl^- ionic complexes. Because of the sizable binding energy (~ 1 eV), it would be difficult to remove H^+/Cl^- pairs from the surface unless the PEALD temperature is substantially high. This implies that the reaction of DCS with surface primary amines, and in turn SiN ALD, can be significantly suppressed by the presence of H^+/Cl^- pairs at relatively low temperatures. The existence of H^+/Cl^- has been confirmed by FTIR measurements which shows two distinctive peaks at 1420 and 2800 cm^{-1}.

SS-TuP-18 Enhancing Fiber-Coupled Thermal Emission Collection Using IR Plasmonic Coating*, **Aman Patel**, R. Kayastha, K. Agyepong, B. Birmingham, Z. Zhang,* Baylor University

Current thermal emission measurement devices have made significant strides in the past few decades but with the current progress of technology towards smaller scale systems, the spatial resolution capabilities of current devices have become inadequate as they utilize the far field emission. The near field emission has orders of magnitude larger signal intensity compared to the far field emission. Current techniques like near field scanning optical microscopy (NSOM) collect the near field emission to improve spatial resolution but remain susceptible to low signal-to-noise ratio. In this experiment, we use titanium nitride (TiN) as an IR-plasmonic coating to enhance the near-field thermal emission collection. Optical fibers were etched to produce different tip geometries, coated with TiN using directed thermal vapor deposition, and put into a furnace to conduct thermal measurements at various temperatures. The collected thermal emissions using the fiber probes before and after TiN coating were compared to analyze the collection of the near field emission. The performance of the plasmonic TiN thin film was compared with a traditional plasmonic metal Au, at temperatures below 600ºC. An increase in signal intensity of the collected thermal emission was observed for fiber tips coated with TiN and with Au. Probes with different TiN coating thicknesses and different tip geometries have been tested to develop a thermal probe with an improved signal-to-noise ratio. The thermal probe is integrated into an NSOM setup, for nanoscale thermal measurements for samples.

SS-TuP-19 The Effects of Surface Treatments on the Nucleation and Growth of Ruthenium on Tantalum Nitride*, C. Feit, U. Kumar, N. Berriel, **Luis Tomar**, S. Seal, P. Banerjee,* University of Central Florida

Ruthenium (Ru) has emerged as an alternative to copper interconnects acting as a diffusion barrier, leading to improved electromigration. Atomic layer deposition is widely used for high-quality, ultra-thin film deposition. However, the deposition of ultra-thin Ru films is challenging. Current Ru ALD processes exhibit island-like grow and long nucleation delays, driven by the surface reactions among sterically bulky precursors, oxidation state of the metal center, and wettability of the substrate. Due to poor nucleation of ruthenium on industrially relevant tantalum nitride (TaN) surfaces, surface engineering is required to reduce Ru liners to competitive widths.

This work examines the effects Ru nucleation and growth, using ruthenium dimethyl butadiene tri-carbonyl (Ru(DMBD)(CO)3) and H2O on ultra-violet ozone treatment of TaN. The film nucleation and surface roughness is measured using atomic force microscopy (AFM). The Ru film thickness is measured by spectroscopic ellipsometry. The surface chemistry is investigated using X-ray photoelectron spectroscopy (XPS) and water contact angle measurements. Furthermore, the thermal conductance and electrical conductance confirm enhance film coalescence. Continuous Ru films can be achieved at ~ 2 nm on UV-ozone treated TaN compared to ~5 nm on untreated TaN.

SS-TuP-20 Laser Assisted Thermal Reactivity of Alkanes on Pt(111)*, Julissa Velasquez,* University of Virginia

A molecular-level understanding of heterogeneous reactions on catalytic surfaces remains to be achieved leading to limitations in improved catalyst design. Alkane dissociative chemisorption on transition metal catalyst surfaces (e.g. Pt, Rh, Cu, etc.) is a key elementary step in alkane reforming providing an important model system to understand surface reaction kinetics and dynamics. The reactivity of a gas phase molecule striking a surface can be described by the molecule's Dissociative Sticking Coefficient (DSC). A DSC describes the probability of a molecule to dissociate on a surface $[RH_{(g)} \leftrightarrow R_{(c)}+H_{(c)}]$. DSCs can be resolved in detail by specifications of temperature (T), energy (E_t, E_v, E_r), and angle (ϑ) of the incident molecules providing enhanced details about the system's kinetics and dynamics. In some instances, DSCs are too small (<10-6) to measure by conventional elemental analysis (Auger Electron Spectroscopy). Instead, it is desirable to study the reactions that produce alkanes in the reverse direction, $[R_{(c)}+H_{(c)} \leftrightarrow RH_{(g)}]$. Laser-assisted thermal associative desorption/Laser activated dissociative desorption (LAAD/LADD) using a 10ns pulsed laser allows for the measurement of the alkane product time-of-flight spectra to a quadrupole mass spectrometer.[1,2] The translational energy distribution, $Pt(E_t)$, of the desorbing alkanes should be identical to the energy distribution of the successfully reacting alkane molecules in the reverse reaction, at the reaction temperature, via the principle of detailed balance.

Implementing this experimental technique required an understanding of the laser's interaction with a Pt single crystal surface. Theoretical laser induced surface temperature jump calculations were used to predict the surface temperature (T_s) rise caused by the laser at a specific pulse energy and beam size.[3] For a thermal reaction, with an Arrhenius rate constant, under fast laser heating a majority of reactivity occurs at the peak surface temperature such that a quasi-isothermal reactivity at the peak temperature (T_s) is achieved. Theoretical work from the Harrison Group has successfully simulated LAAD experiments for $[CH_{3(c)}+H_{(c)} \leftrightarrow CH_{4(g)}]$ on Pt(111)[4] and Ru(0001)[2]. Here we present experimental limits for Nd:YAG laser to avoid surface damage or induce alteration to the desorbing flux. The first implementation of the LAAD/LADD experimental technique in our lab has been to look at the laser assisted thermal desorption of methane $[CH_{4(ad)} \rightarrow CH_{4(g)}]$ by measuring the methane $Pt(E_t)$, which is expected to roughly be a flux-weighted Maxwell-Boltzmann distribution at the desorption temperature.

SS-TuP-21 ID31 - High-Energy Beamline at ESRF for Buried Interface Structure and Materials Processing*, Andrea Sartori,* *J. Drnec,* ESRF, France

Complex heterogeneous materials, and their interfaces, inside operating devices can only be studied adequately by combining experimental methods to reveal the interplay between the microscopic material/interface properties and the macroscopic device performances. The need for combining techniques is instrumental in the development of hard x-ray synchrotron methods applied in situ and operando for studying both real devices under operating conditions and idealized model systems under precisely controlled environments.
The high energy beamline ID31 of ESRF, dedicated for studies of buried surfaces and interfaces, enables a portfolio of hard x-ray characterization techniques, including reflectivity, wide angle diffraction both in transmission and grazing incidence geometry, small angle x-ray scattering, and imaging methods coupled with great versatility in choosing beam sizes (minimum: horizontal 20.0 x vertical 3.0 µm², maximum horizontal: 2.0 x vertical 1.0 mm²), energy range (21.0 – 150 keV) and detectors optimized for high energy x-rays. The design enables many different studies with remarkable potential. More details about the beamline are reported in the supplemental file.
In this contribution we will discuss the design and the capability of the beamline, together with example of in situ experiment in the field of liquid organic hydrogen carrier (LOHC). By using high energy X-Ray diffraction to study the dehydrogenation reaction of benzyltoluene. We investigated, at atomic resolution, a catalyst of single crystal Al_2O_3 sample supporting Pt nanoparticles. The experiments were performed in a custom-made reactor in operando under realistic conditions (260 °C, 1.5 bar). The first results show an increase of the full width half maximum and the shift of the Pt (111) peak suggesting possible formation of a carbide in the nanoparticles surface, extended more than just one monolayer. Further characterization and experiments are in progress.

SS-TuP-22 Modeling Surface Interactions: Methods and Select Applications*, Sierra Jubin,* Princeton University*; Y. Barsukov,* Princeton Plasma Physics Laboratory*; I. Kaganovich,* Princeton Plasma Physcis Laboratory

Though molecular dynamics (MD) is a powerful tool for investigating materials properties, one must take great care that the MD potentials properly represent the system of interest. The modeling of surface interactions presents a particularly difficult challenge. MD potentials which reproduce bulk properties may fail to predict energies and geometries related to the adsorption and reaction of atoms and molecules on the surface. For example, our MD simulations showed that bond order MD potentials which have been used to describe amorphous boronized graphite yield highly unrealistic models of boron adsorption on a graphene sheet [1].

For systems where suitable MD potentials are not available or lead to questionable results, the DFTB MD (density functional tight binding molecular dynamics) method might be used. Note that DFTB is a semi-empirical parameterized method, and parameter sets exist for a limited number of chemical systems. Moreover, there is no guarantee that DFTB parameters for a set of elements give the correct structures of all possible compounds consisting of this set of elements. For example, available DFTB parameter sets can describe the geometry of stable NH_3 and HF molecules, but do not predict the existence of salts with an ammonium cation, such as $NH_4^+F^-$ and $NH_4^+HF_2^-$. For such complex systems, the Car-Parrinello MD method can be used rather than DFTB. Another issue with MD methods can occur in chemical reactions proceeding via a significant barrier, because the simulation time required to overcome the barrier may be prohibitively long. Nonetheless, our group has used DFTB MD to successfully explore the formation of BN chains and fulborenes by self-assembly [2].

A powerful method for the study of chemical reactions with large energy barriers is the use of DFT (density functional theory) in conjunction with transition state theory, which can predict the probabilities of elementary steps in surface reactions. Often, the rate of a whole reactions is limited by the rate of the slowest elementary step within that reaction. For example, using DFT modeling we showed that F_2 dissociative adsorption on a fluorinated Si surface leads to Si-Si bond breaking, following a reaction pathway that proceeds over a barrier. Thus, the rate of Si etching by F_2 can be calculated as a function of F_2 partial pressure and temperature. This modeling also demonstrated that the rates of F_2 dissociative adsorption on (111), (110) and (100) oriented Si surfaces are significantly different at room temperature.

[1] S Jubin *et al* 2022 *Frontiers in Physics***10** DOI: 10.3389/fphy.2022.908694

[2] Y Barsukov *et al* 2021 *Nanotechnology***32** 475604 DOI: 10.1088/1361-6528/ac1c20

SS-TuP-24 Deterministic Switching Using Unconventional Spin-Orbit Torques in Atomically Clean WTe_2/FGT Heterostructures*, Sean Yuan,* *I. Kao, R. Muzzio,* Carnegie Mellon University*; J. Edgar,* Kansas State University*; J. Goldberger,* Ohio State University*; J. Yan,* Oak Ridge National Laboratory*; J. Hwang,* Ohio State University*; J. Katoch, S. Singh,* Carnegie Mellon University

Layered materials with low-symmetry crystal structure, such as WTe_2 and $MoTe_2$, are energy efficient spin source materials for spintronics-based memory and logic devices. We will present results showing the fabrication of spin-orbit torque (SOT) switching devices constructed out of vdW based heterostructures with atomically clean interfaces. The sharpness of the interface is essential to suppress interfacial spin dephasing, and thus enhance SOT efficiency for spintronics applications. Here, we present results showing the fabrication of SOT switching devices with atomically sharp interfaces, which we construct to enable SOT-driven deterministic control of a magnet with out-of-plane polarization[1]. This is challenging because deterministic field-free switching of a perpendicularly polarized ferromagnet requires an out-of-plane anti-damping torque, which is typically prohibited due to in-plane crystal symmetries within conventional spin sources. In order to achieve this unconventional SOT form, we exploit the low in-plane crystal symmetries of WTe$_2$, enabling an out-of-plane SOT component[2,3]. This work is the first step towards realizing all-vdW based spintronic devices that are ultra-thin and have ultra-low power consumption for their operation.

1. Kao, IH., *et al*., *Nat. Mater.* 21, 1029–1034 (2022).

2. D. MacNeill *et al.,Nat. Phys.* 13, 300 (2017)

3. F. Xue *et al.,Phys. Rev. B* 102, 01440 (2020)

SS-TuP-25 Preparing and Characterizing Thin Hexagonal Boron Nitride Flakes for Creating Spin Defects*, Seth Eisenberger*, *I. Kao, R. Muzzio, J. Katoch, S. Singh,* Carnegie Mellon University

Spin defects in layered van der Waals systems, such as hexagonal boron nitride (h-BN), is an appealing platform for quantum sensing. In this work, we will discuss the preparation and characterization of atomically thin flakes of h-BN using different experimental methods including Raman spectroscopy and atomic force microscopy. We have successfully coupled h-BN flakes to on-chip micro coplanar waveguides and have created atomic defects in h-BN using high energy ion implantation. We will also discuss methods for transferring h-BN flakes onto scanning transmission electron microscopy grids for characterizing these defects.

SS-TuP-26 Visualizing the Electronic Structure of Multiple Twisted Bilayer Graphene Domains*, Indra Periwal*, *R. Muzzio,* Carnegie Mellon University*; C. Jozwiak, A. Bostwick, E. Rotenberg,* Lawrence Berkeley National Laboratory*; S. Singh, J. Katoch,* Carnegie Mellon University

Twisted two dimensional (2D) heterostructures have emerged as a novel way to modulate the physical properties of matter, the most famous of which is the unconventional superconductivity in twisted bilayer graphene (twBG). It is therefore essential to determine the evolution of twisted bilayers as we vary the twist angle. In this study, we employ nano-focused angle resolved photoemission spectroscopy (ARPES) to investigate twBG over a wide range of twist angles. We will discuss the heterostructure fabrication, momentum-resolved measurement, and 4-dimensional analysis of our sample which contains various twBG domains. Each domain contains a different twist angle and we will discuss the implications of the change in the electronic structure.

SS-TuP-27 Angle-Resolved XPS Analysis of the Oxidation of Ru Thin Films*, Shivan Antar*, *A. Valenti, R. Wheeler, C. Ventrice,* SUNY Polytechnic Institute*; M. Strohmayer, J. Brewer, C. Nassar, C. Keimel,* Menlo Micro

Ruthenium is often used as an electrical contact material because of its resistance to oxidation at elevated temperatures. In addition, the most stable stoichiometry of ruthenium oxide under ambient conditions is RuO$_2$, which is an electrically conductive oxide. The goal of this study is to determine the stoichiometry and measured thickness of the surface oxide on Ru formed by various and typical semiconductor fabrication processing techniques such as reactive ion etch, plasma ashing processes, silicon dioxide depositions, and annealing in various environments. The primary analysis technique used for this study is X-ray photoelectron spectroscopy (XPS). The Ru thin films were deposited on SiO$_2$/Si(100) substrates. Angle-resolved XPS data were collected at takeoff angles of 10°, 20°, 30°, 40°, 50°, and 60°, where the takeoff angle is measured from the plane of the surface. The acceptance angle of each of the angle-resolved measurements was 10°. Angle-integrated XPS data were collected at a takeoff angle of 45° and acceptance angle of 40°. Analysis of the Ru-3d XPS spectrum of the as-grown Ru film indicates that the native oxide is in a 2+ state and is less than a nm thick. Annealing at atmosphereic pressure results in the formation of Ru in a 4+ state (RuO$_2$) at the surface that is ~2 nm thick. In addition, the presence of higher order oxides and surface carbon is detected after the anneal. Performing either a RIE or ash process on the as-deposited Ru film also results in the formation of RuO$_2$ but with a thickness of ~1 nm. Higher order oxides (RuO$_x$) and carbon are also present in the surface region after these processing techniques have been performed but at a lower surface concentration than the sample annealed in air. Analysis of the O-1s XPS spectra of the samples indicates the presence of an ~1 nm thick water layer on top of each sample during the measurements.

This project is funded in part by the New York State Center for Advanced Technology in Nanomaterials and Nanoelectronics (CATN2).

Vacuum Technology Division
Room Ballroom A - Session VT-TuP
Vacuum Technology Poster Session

VT-TuP-1 Analysis and Quantification of the Impurities in a 300mm Etch Tool Exhaust During an Oxide Etch Process with CF4 Under Plasma*, Anup Kumar Doraiswamy*, *C. Jennings,* Air Liquide*; N. Stafford,* air liquide*; P. Nguyen,* Air Liquide

The consumption of the etching gases, primarily perfluorocarbons, is expected to significantly increase in the near future to match the increasing demand of electronic devices. While the global warming potential (GWP) from the direct emission of these perfluorocarbons (PFCs) is known, the quantity and identity of the species generated from them in the etch chamber may not be well understood. These plasma generated species can also have high GWP, contributing to the greenhouse effect in addition to being detrimental to the air quality by affecting COX NOX levels, etc. Therefore the identification, quantification and abatement of these compounds is of increasing interest to both semiconductor manufacturers and environmental regulators. Our current study focuses on analyzing and quantifying the exhaust of a 300 mm commercial etch tool during an oxide etch process using standard etching chemistry such as CF4. In our experiments, the plasma etch tool has been supplemented with a quadrupole mass spectrometer (Q-MS) and infrared spectrophotometer (FTIR) to identify and quantify the concentration of species in the exhaust generated from the plasma etching process.

VT-TuP-2 Amorphous Carbon Thin Films: Influence of Hydrogen Contamination on the Secondary Electron Emission Properties*, Carolina Adame*, CEFITEC, NOVA School of Science and Technology, Portugal*; E. Alves, N. Barradas,* DECN and IPFN, Instituto Superior Técnico, University of Lisbon, Portugal*; N. Bundaleski,* CEFITEC, NOVA School of Science and Technology, Portugal*; P. Pinto,* CERN, Switzerland*; J. Deuermeier,* CENIMAT|i3N, NOVA School of Science and Technology and CEMOP/UNINOVA, Portugal*; Y. Delaup,* CERN, Switzerland*; I. Ferreira,* CENIMAT|i3N, NOVA School of Science and Technology and CEMOP/UNINOVA, Portugal*; H. Neupert, M. Himmerlich , S. Pfeiffer, M. Rimoldi, M. Taborelli,* CERN, Switzerland*; O. Teodoro,* CEFITEC, NOVA School of Science and Technology, Portugal

One of the major limitations for the luminosity of modern particle accelerators is the formation of electron clouds (e-clouds), which cause beam instabilities, rise in pressure and thermal load to the system. The formation of electron clouds start with seeding electrons that originate in residual gas ionization (by the beam) or photoemission (from the wall, induced by synchrotron radiation). The seeding electrons are multiplied in an avalanche process induced by electron acceleration towards the walls by the beam potential, eventually creating an e-cloud.

One strategy to reduce the formation of e-clouds, successfully applied at CERN, is coating of the accelerator walls with amorphous carbon (a-carbon), having low Secondary Electron Yield (SEY). However, in some cases the coatings may become contaminated by hydrogen during the deposition, causing SEY growth above the threshold for e-cloud formation. In this work we explore the mechanism behind the change of secondary electron emission properties of a-carbon coatings due to hydrogen contamination.

a-carbon coatings were produced on Si and quartz substrates by magnetron sputtering with different amounts of D$_2$ added to the Ar discharge gas, to study the influence of these contaminations on SEY and resolve it from the natural contamination by hydrogen. In addition to SEY measurements, the samples were characterized by Elastic Recoil Detection Analysis (ERDA), X-ray Photoelectron Spectroscopy (XPS) and Optical Absorption Spectroscopy (OAS), providing information about their elemental, phase composition, and electronic structure.

The relative amounts of deuterium and hydrogen from the residual gas incorporated into the a-carbon thin films was quantified by ERDA. This incorporation increased SEY, and contributed to the deposition of non-uniform films, consisting of graphitic, diamond-like and hydrocarbon phases (as revealed by XPS). The SEY and optical energy gaps (determined using Tauc plots) increase with the amount of incorporated deuterium. The latter seem to be related with the amount of the graphitic phase in the samples: samples with higher graphitic-carbon fractions have lower SEY and higher light absorption, showing that graphitic regions work as energy absorbers for both light and secondary electrons. Increase of hydrogen species in the samples reduces the graphitic content, thus increasing SEY and light transmission.

2D Materials Technical Group
Room 303 - Session 2D+EM+MI+NS+QS-WeM

2D Materials: Quantum and Symmetry-Protected States

Moderators: Thomas Michely, University of Cologne, Germany, **Frances Ross**, Massachusetts Institute of Technology

8:00am **2D+EM+MI+NS+QS-WeM-1 Semi-High Throughput Investigation of 2d Materials: Anomalous Quantum Confinement Effect and Spectral Properties***, **Francesca Tavazza**, K. Choudhary,* National Institute of Standard and Technology **INVITED**

Materials with van der Waals-bonding exhibit quantum confinement effect, in which the electronic bandgap of the three-dimensional (3D) form is lower than that of its two-dimensional (2D) counterpart. However, the possibility of an anomalous quantum confinement effect (AQCE) exists, where the bandgap trend is reversed. In this work, we computationally identify materials with AQCE. Using density functional theory (DFT), we compute ≈1000 OptB88vdW (semi-local functional), ≈50 HSE06 and ≈50 PBE0 (hybrid functional) bandgaps for bulk and their corresponding monolayers, in the JARVIS-DFT database. OptB88vdW identifies 65 AQCE materials, but the hybrid functionals only confirm such finding in 14 cases. Electronic structure analysis shows that AQCE is often characterized by the lowering of the conduction band in the monolayer and related changes in the p_z electronic orbital contribution. In addition to AQCE, the JARVIS-DFT contains IR and Raman spectra for many 2D materials. Properties of such spectra will be discussed as well.

8:40am **2D+EM+MI+NS+QS-WeM-3 Dry Patterning Chemically Sensitive Quantum Materials***, **Joseph Benigno**, Q. Zou, C. Cen, L. Li,* West Virginia University

Accurate, repeatable patterning of quantum material-based electronic devices is desirable for electrical transport measurements. However, the most common method, photolithography, can degrade, or even damage, chemically sensitive quantum materials during fabrication. Here we introduce a new dry-patterning method for device fabrication with lateral etching resolution down to ~30 µm. The new method utilizes a tabletop computer numerical control (CNC) router machine to gently etch patterns into thin films, leaving behind the desired device or devices on the substrate. We create Hall bars with conductive channel widths of 30, 60, and 120 µm from ~20 layer FeTe-capped superconducting single layer FeSe/$SrTiO_3$ systems. Transport measurements show the same zero resistance T_c of 10 K for the Van der Pauw (vdP) geometry and all Hall bar structures. However, the onset temperature T_{onset} is the largest at 28K for the vdP geometry, and decreases with the width of the Hall bar to 13K for the 60 µm device. Our method provides a new time-saving, cost-effective, and chemical-free strategy for fabrication of devices from quantum materials.

This research is supported by DOE DE-SC0021393.

9:00am **2D+EM+MI+NS+QS-WeM-4 Electron Transport and Charge Sensing in Strongly Coupled Quantum Dot Array in Silicon***, **Fan Fei**, J. Wyrick, P. Namboodiri, J. Fox,* NIST*; E. Khatami,* SJSU*; R. Silver,* NIST

Atomically precise donor-based quantum devices in silicon are fabricated using STM lithography, which has become a promising platform for solid state quantum computation and analog quantum simulation. Lattices of dopant-based quantum dots have unique advantages in simulating strongly correlated Fermionic systems of real atomic lattice sites because of their naturally occurring ion-cores which make them the Fermi-Hubbard sites in the Silicon Vacuum. Understanding electron transport and charge configuration in a smaller array is critical to using these arrays to simulate larger systems and explore various condensed matter physics phenomena such as superconductivity in the future. This talk will focus on the electron transport in the strongly coupled regime where the electrons delocalize across small N x N dot arrays. Numerical simulations for charge stability diagrams and transport properties show qualitatively agreement with our experiments. We apply rf reflectometry on a SLQD and use it as charge sensor for probing the electron configuration within the array.

9:20am **2D+EM+MI+NS+QS-WeM-5 Observation of the Layer Hall Effect in Topological Axion Antiferromagnet $MnBi_2Te_4$***, **Suyang Xu**,* Harvard University **INVITED**

While ferromagnets have been known and exploited for millennia, antiferromagnets were only discovered in the 1930s. The elusive nature indicates antiferromagnets' unique properties: At large scale, due to the absence of global magnetization, antiferromagnets may appear to behave like any non-magnetic material; At the microscopic level, however, the opposite alignment of spins forms a rich internal structure. In topological antiferromagnets, such an internal structure leads to a new possibility, where topology and Berry phase can acquire distinct spatial textures. We study this exciting possibility in an antiferromagnetic Axion insulator, even-layered $MnBi_2Te_4$ flakes. We report the observation of a new type of Hall effect, the layer Hall effect,where electrons from the top and bottom layers spontaneously deflect in opposite directions.

Reference:

A. Gao, et al."Layer Hall effect in a 2D topological axion antiferromagnet." *Nature* 595, 521 (2021).

11:00am **2D+EM+MI+NS+QS-WeM-10 Phonon Limited Mobility and Phonon Drag in h-BN Encapsulated Monolayer and AB-stacked Bilayer Graphene***, **Vasili Perebeinos**,* University at Buffalo

We report the electrical transport in h-BN encapsulated AB-stacked bilayer graphene theoretically and experimentally. Using the perturbation theory within the tight-binding model approach, we identify the dominant role of the shear phonon mode scattering on the carrier mobility in AB-stacked graphene bilayer at room temperature. The shear phonon mode is absent in free-standing monolayer graphene, which explains high mobilities in monolayer devices fabricated under similar conditions resulting in minimal Coulomb impurity scattering. At temperatures above 200K, the surface polar phonon scattering from the boron-nitride substrate contributes significantly to the experimental mobilities of 15,000 -20,000 cm^2/Vs at room temperature and carrier concentration $n\sim10^{12}$ cm^2 reported here. A screened SPP potential for a dual gated bilayer and transferable tight-binding model allows us to predict mobility scaling with temperature and bandgap for both electrons and holes in agreement with the experiment Phys Rev. Lett. 128, 206602 (2022).

The resulting electron-SPP coupling is used to predict that, by exploiting the strong coupling of their electrons to surface polar phonons, van der Waals heterostructures can offer a suitable platform for phonon sensing, capable of resolving energy transfer at the single-phonon level. The geometry we consider is one in which a drag momentum is exerted on electrons in a graphene layer, by a single out-of-equilibrium phonon in a dielectric layer of hexagonal boron nitride, giving rise to a measurable induced voltage. Our numerical solution of the Boltzmann Transport Equation shows that this drag voltage can reach a level of a few hundred microvolts per phonon, well above experimental detection limits. Furthermore, we predict that drag voltage should be largely insensitive to the mobility of carriers in the graphene layer and increase the temperature up to at least 300 K, offering the potential of a versatile material platform for single-phonon sensing.

11:20am **2D+EM+MI+NS+QS-WeM-11 Exciton Physics at the Atomic Scale***, **Daniel Gunlycke**,* U.S. Naval Research Laboratory

Descriptions of excitons in pristine semiconducting crystals usually rely on the hydrogen model adopted for excitons. Owing to the weak screening in monolayer transition-metal dichalcogenides, however, the electron and hole separation in the strongest bound excitons is on the atomic scale, necessitating atomistic treatment. In this presentation, we present a minimalistic exciton model that accounts for the lattice and the spin-orbit and exchange interactions, thus making this model appropriate across the spectrum from Wannier to Frenkel excitons. Using this model, we show that the exciton lifetimes could be extended by transitioning the excitons into excitonic dark states. Longer exciton lifetimes could make these materials candidates for applications in energy management and quantum information processing.

11:40am **2D+EM+MI+NS+QS-WeM-12 Weyl Semimetals with Low-Symmetry Crystal Structure for Generating Out-of-Plane Oriented Spin Current***, **Simranjeet Singh**,* Carnegie Mellon University **INVITED**

Weyl semimetals (WSMs), such as WTe_2 and $MoTe_2$, host plethora of novel phenomena that are highly relevant for quantum spintronics, namely: Dirac type dispersion, strong spin-orbit coupling (SOC), Fermi arcs, and helical spin-momentum locked surface and bulk states. WSMsprovide a distinct opportunity to obtain highly efficient and unconventional charge to spin conversion owing to strong SOC, symmetry breaking, and these topology-based phenomena. On the other hand, spin-orbit torque (SOT) driven deterministic control of the magnetic state of a ferromagnet with perpendicular magnetic anisotropy is key to next generation spintronic applications including non-volatile, ultrafast, and energy efficient data storage devices. But field-free deterministic SOT switching of perpendicular magnetization remains a challenge because it requires an out-of-plane oriented spin current, which is not allowed in conventional spin source materials such as heavy metals and topological insulators due to the system's symmetry. The exploitation of low-crystal symmetries WTe$_2$ and MoTe$_2$ offers a unique approach to achieve SOTs with unconventional forms[1]. In this work, I will discuss our experiments to realize field-free deterministic magnetic switching of a perpendicularly polarized van der Waals magnet employing an out-of-plane spin current generated in layered WTe$_2$, which is a quantum material with low-symmetry crystal structure[2]. I will also discuss our experiments aimed at achieving field-free SOT switching of semiconducting and insulating FMs using spin current in WSMs. Our work establishes transition metal dichalcogenides, with lower symmetry crystal structure, as an appealing spin source material for future spin-orbit torque related magnetic memory technologies.

[1]. MacNeill, D. *et al.* Control of spin–orbit torques through crystal symmetry in WTe$_2$/ferromagnet bilayers. *Nature Physics***13**, 300-305, (2017).

[2]. Kao, I-H *et al.* Deterministic switching of a perpendicularly polarized magnet using unconventional spin–orbit torques in WTe$_2$. Nature Materials (2022). https://doi.org/10.1038/s41563-022-01275-5

Actinides and Rare Earths Focus Topic
Room 318 - Session AC+LS+MI-WeM

Magnetism, Electron Correlation, and Superconductivity in the Actinides/Rare Earths

Moderators: James G. Tobin, University of Wisconsin-Oshkosh, **Ladislav Havela**, Charles University, Czech Republic, **Gertrud Zwicknagl**, Technical University Brauschweig, Germany

8:00am **AC+LS+MI-WeM-1 The Relation between Crystal Chemistry and Superconductivity in Actinide-Based Superconductors*, Eteri Svanidze,*** Max Plank Institute, Dresden, Germany **INVITED**

Crystallographic features play an important role in the physical and chemical properties of a given solid-state material. In particular, actinide-based systems exhibit a wide range of properties – from unconventional superconductivity to peculiar magnetic orders. In this talk, I will highlight some of the old and new actinide-based superconductors, in which a delicate interplay between chemistry and physics is observed. A comprehensive characterization of properties of UBe$_{13}$ has revealed a deep interrelation between the physical and chemical features. Notably, single crystals of this material tend of include many defects which have a dramatic effect on superconducting state [1]. Motivated by this issue, an alternative method of studying intrinsic properties is investigated [2-4]. By creating a micro-scale device, it is possible to measure intrinsic superconductivity of UBe$_{13}$, whichhas so far remained out of reach [4]. The properties of UBe$_{13}$ are compare to those of other actinide-based superconductors – UTe$_2$ [5] and Th$_4$Be$_{33}$Pt$_{16}$ [6] – in which a strong coupling of lattice and superconducting properties is observed. By studying these systems, it is possible to expand the understanding of crystal chemistry of solid-state materials, while simultaneously providing an insight into which crystallographic parameters impact the physical properties of a given solid-state material.

[1] A. Amon *et al.*, "Tracking aluminium impurities in single crystals of the heavy-fermion superconductor UBe$_{13}$,"*Sci. Rep.***8**, 10654 (2018)

[2] E. Svanidze *et al.*, "Revealing intrinsic properties of UBe$_{13}$", *in preparation* (2022)

[3] A. Amon *et al.*, "Interplay of atomic interactions in the intermetallic semiconductor Be$_5$Pt", *Angew. Chem. Int. Ed.***58**, 2 (2019).

[4] I. Antonyshyn *et al.*, "Micro-scale device - an alternative route for studying the intrinsic properties of solid-state materials: case of semiconducting TaGeIr", *Angew. Chem. Int. Ed.***59**, 2 (2020)

[5] E. Svanidze *et al.*, "Intrinsic crystal structure of UTe$_2$", *in preparation* (2022)

[6] P. Kozelj *et al.*, "A noncentrosymmetric cage superconductor Th$_4$Be$_{33}$Pt$_{16}$", *Sci. Rep.***11**, 22352 (2021)

8:40am **AC+LS+MI-WeM-3 Revealing The Beauty of Uranium Compounds:the UMB$_4$ (M=V, Cr, Fe, Co, Mo, W, Re, Os) and UFe$_x$Sb$_2$ Cases*, Antonio Pereira Gonçalves,*** Instituto Superior Técnico, Univ. Lisboa, Portugal **INVITED**

Uranium-based phases with d-metals show a vast and rich variety of physical properties, some of them unique, which are mainly driven by the large 5*f* spin-orbit coupling and the degree of delocalization of the 5*f* states. The understanding of such behaviors is critical for the advance of Solid State Sciences and can lead to the discovery of new phenomena and ground states. In this talk, examples of uranium compounds with unusual properties are presented, the focus being on UMB$_4$ materials and UFe$_x$Sb$_2$ alloys.

UMB$_4$ (M=V, Cr, Fe, Co, Mo, W, Re, Os) compounds are quite notable, crystallizing in the YCrB$_4$-type (for V, Cr, Fe, Co) and ThMoB$_4$ type (for Mo, W, Re, Os) polymorphs. Both structures are closely related, containing the same number of atoms in the unit cell and similar coordination polyhedral, which allows the comparison of their properties as a function of the d-metal. Their electronic structure is influenced by a strong hybridization between the B-2*p* states and both the *d*-metals *d*-states and the uranium (5*f*) valence band states. This avoids the formation of narrow bands with high density of states at the Fermi level, even if the 5*f*-*d* hybridization is weak, i.e. for late d-metals. Hence, the explored UMB$_4$ compounds are weak Pauli paramagnets, with a density of states at Fermi level of only ~4 times higher than for α-U. Those crystalizing in the ThMoB$_4$ structure show anomalous lattice vibrations, in particular the presence of low-energy Einstein modes, which can lead to superconducting ground states.

UFe$_x$Sb$_2$ alloys crystallize in the HfCuSi$_2$ type structure and present a remarkable ground state evolution with Fe concentration. UFe$_{0.5}$Sb$_2$ shows a non-Fermi liquid behavior, with a change from metallic to semiconductor-upon applying magnetic field. In contrast, UFe$_{0.7}$Sb$_2$ (and, in a minor scale, UFeSb$_2$), shows an increase in electrical resistivity with decreasing temperature under zero magnetic field, but for high magnetic fields a metallic behavior is established. First principles calculations indicated that in UFeSb$_2$ some bands cross the Fermi level, but they are relatively steep and, as a result, the density of states at Fermi level is low, which supports the semi-metallic character of this composition. In the case of UFe$_{0.5}$Sb$_2$, a higher concentration of bands at the Fermi level, some of them relatively flat, exist, which cause a sudden step-shaped drop of density of states just above Fermi level. The magnetic field application can raise the Fermi level into the pseudo-gap, which is probably the reason for the change from a metallic-like to a semiconductor-like behavior.

11:00am **AC+LS+MI-WeM-10 Uranium Hydrides Revisited*, Ladislav Havela,*** Charles University, Faculty of Mathematics and Physics, Czechia*; D. Legut,* VSB Technical University Ostrava, Czechia*; J. Kolorenc,* Institute of Physics, Czech Academy of Sciences, Czechia

Uranium hydrides are not only materials important for understanding of fundamental aspects of actinides. They are also relevant for nuclear technologies as well as for specific hydrogen storage tasks, as e.g. storing of tritium in nuclear fusion devices. Electronic structure of uranium hydrides (α- and β-UH$_3$, UH$_2$) reflects two contradictory tendencies. One is a charge transfer from U towards H, the other is a stability of the *f* shell. The latter is illustrated also on the case of rare earth hydrides with anomalous rare earth elements, such as Yb or Eu, which surprisingly retain their lower valence state, i.e. with a higher *f*-occupancy. The transfer is thus realized in U by the 6*d* and 7*s* electrons, which become noticeably depleted, but the 5*f* occupancies remain high. The concomitant reduction of the 5*f*-6*d* hybridization contributes, together with the volume expansion, to pronounced ferromagnetism of the U hydrides with Curie temperatures far above 100 K. We compare individual hydrides described by the GGA+*U* calculations, yielding numbers on the charge transfer or spin and orbital moments, with relevant experimental data. Interesting feature obtained from calculations is that the two different U sites in β-UH$_3$ have the respective magnetizations non-collinear. The same calculations yield also phonon dispersion relations, which are used to determine the temperature dependence of phonon contribution to heat capacity. The agreement in the paramagnetic range is so good that it allows to determine both the magnetic entropy and changes of the Sommerfeld coefficient between the ground state and paramagnetic state, the latter being twice higher. The position of the U hydrides on the map of localization-delocalization dichotomy will be discussed.

The work was supported by the Czech Science Foundation under the grant No. 21-09766S.

11:20am **AC+LS+MI-WeM-11 Towards a Better Understanding of the Rkky Interaction in Ce- and Yb-Based Compounds: Anisotropies from Cef Effects and Fermi Surfaces**, ***Gertrud Zwicknagel,*** Institut für Mathematische Physik, Germany*; V. Zevin,* The Racah Institute of Physics, Israel

We calculate the influence of Crystalline Electric Field (CEF) effects and the Fermi surface topology on the indirect Ruderman-Kittel-Kasuya-Yoshida (RKKY) exchange interaction between local 4f moments in Ce- and Yb-compounds. Starting from a periodic Anderson model, we show that the anisotropy of the CEF ground state manifests itself in the anisotropy of the effective exchange coupling constant J(R,R′) between two moments at sites R and R′. If spin-orbit effects among the conduction states can be neglected, the interaction between two Kramers doublets is isotropic in pseudo-spin space. Adopting the Stationary Phase approach, we derive the asymptotic form of the exchange constant for arbitrary Fermi surfaces. We evaluate the anisotropy of the RKKY interaction in tetragonal Ce- and Yb-122 compounds for realistic model bands. The influence of spin-orbit interaction among the conduction electrons is discussed.

11:40am **AC+LS+MI-WeM-12 Mechanically Forced Tuning of Interactions in Tetragonal 221 Intermetallics**, ***Petr Král,*** *J. Prchal,* Charles University, Czech Republic*; J. Kaštil,* Czech Academy of Sciences, Czech Republic*; D. Daisenberger,* Diamond Light Source, UK*; D. Staško,* Charles University, Czech Republic

Family of R_2T_2X intermetallics adopting the tetragonal Mo_2FeB_2-type crystal structure represents the group of anisotropic systems with potential to exhibit geometrical frustration effects due to the Shastry-Sutherland-like arrangement of *R*-atoms in the aa-planes alternated by usually non-magnetic *T-X* planes along the crystallographic *c*-axis. Crucial for resulting magnetic behavior are the interatomic distances affecting the exchange interactions between individual ions. Especially interesting may be the compounds close to the empirical boundary of crystal structure stability since, based on available data, the lowest observed unit-cell volume among Mo_2FeB_2-type materials is about $V_{\mathrm{f.u.,crit}} = 200$ Å^3.

The unique tool allowing to act directly on the interatomic distances without changes of chemical composition is mechanical pressure. Employing the high-pressure techniques, it is possible to influence all lattice-related physical properties including e.g. the magnetic interactions and electronic structure. Especially in the strongly anisotropic compounds, the hydrostatic pressure effect depends on the compressibility of individual lattice parameters. This is the case, when the uniaxial pressure may represent the opportunity to act selectively in chosen crystallographic directions and thus to provide the insight into the layout of interactions within the crystal lattice.

Herewith, we are presenting the results of systematical study of pressure impact on the R_2T_2X compounds. Special attention is paid to Ce_2Pd_2In considered to be one of the most interesting systems among R_2T_2X family. It represents the rare example of Ce-based ferromagnet, however the ground state is reached through the antiferromagnetic interphase. High sensitivity of magnetic behavior to hydrostatic pressure has been revealed showing the preference of antiferromagnetic phase at lower pressures followed by the Kondo-like anomaly formation and suppression of magnetic ordering at pressures around 4 GPa. Based on the results of high-pressure XRD experiment, the hydrostatic pressure acts more significantly within the basal plane. Indeed, different response to the uniaxial pressure applied along the *c*-axis was observed.

Compounds with the unit-cell volume closest to $V_{\mathrm{f.u.,crit}}$ belongs to the series R_2Cu_2In. Among them the ferromagnets Dy_2Cu_2In (exhibiting the signs of spin-reorientation at lower temperatures) and Tm_2Cu_2In (with signs of spin-glass behavior) were investigated. Concerning the later one, the pressure was found to support the frustration effects responsible for the spin-glass properties as the unit-cell volume tends to reach the $V_{\mathrm{f.u.,crit}}$.

12:00pm **AC+LS+MI-WeM-13 Effects of O_2 Growth Pressure on the Magnetization of $LaMnO_3$-$SrTiO_3$ Thin Films**, ***Ghadendra Bhandari,*** West Virginia University*; R. Trappen,* University of Waterloo*; N. Mottaghi, M. Holcomb,* West Virginia University

Magnetic properties of epitaxial $LaMnO_3$ thin films grown on $SrTiO_3$ substrate have been studied. Thin films are grown at various oxygen pressure using pulsed laser deposition and deposition has been monitored by reflection high energy electron diffraction (RHEED) to verify layer-by-layer growth. Bulk stoichiometric $LaMnO_3$ exhibits A-type antiferromagnetic order, whereas thin films show a ferromagnetic FM phase. Structure and magnetic properties have been characterized by X-ray diffractometry (XRD), X-ray reflectivity (XRR) and vibration sample magnetometry (VSM). The thin films are showing ferromagnetic (FM) phase. Depth dependent magnetization studied by polarized neutron beam reflectivity found that magnetization is higher near interfacial region and a magnetically dead region lies at the surface. We have observed c-lattice correlated magnetization, which is minimized at 30mTorr O_2 pressure.

Applied Surface Science Division
Room 320 - Session AS+BI+CA+HC+LS+PS+SE+SS-WeM

Analysis of Surfaces and Interfaces Related to Energy and the Environment

Moderators: Kateryna Artyushkova, Physical Electronics, **Tony Ohlhausen**, Sandia National Laboratory

8:00am **AS+BI+CA+HC+LS+PS+SE+SS-WeM-1 Adhesion Properties of Industrial Steel Samples**, ***Lukas Kalchgruber****, M. Hahn, L. Mears, M. Valtiner,* TU Wien, Austria

Solving industrial questions is of utmost importance to improve material properties, developing industrial applications and understanding fundamental processes. One of these questions is how different pre-treatments alter the adhesion process between steel and polymers.

To study the effect of the pre-treatment on the subsequent adhesion process, steel was treated either thermally or via plasma.

To characterize adhesion, the surface force apparatus (= SFA) was utilized in reflection mode. In the SFA experiment, the steel is brought into contact with another surface which is prepared on a fused silica optical disc. Before the optical discs can be used in SFA, a semitransparent, reflective layer needs to be deposited on the curved surface. Additionally, they were spin coated with few µm thin, homogeneous, smooth layers of SEBS polymer. Afterwards, a suitable particle free contact was established between the polymer and the steel sample in the SFA, which generated the following data types:

- Newton rings à Provide information about the contact area
- Force data à Adhesive pressure (referenced to contact area)
- Fringes of chromatic order (= FECO) à Time-Distance-Curves

The main selling points of this technique are as follows: firstly, the model system is very close to the actual problem, as the steel sample in question can be used directly. Secondly, direct information about the adhesive pressure can be obtained. Thirdly, considerably more information about the adhesive behavior of the system is available beyond just one number.

The SFA results achieved are promising. We have a method that allows us to quantify the adhesive pressure in a model system and differentiate between differently treated steel samples. We have further put our adhesion results into context with the support of XPS characterization of the surface. Thermally treated samples have a hydroxide/oxide ratio of roughly 50/50 while samples treated with plasma show a ratio of 90/10. The hydroxide to oxide ratio correlates with the adhesion measured by SFA, which emphasizes the role of hydroxide in preventing adhesion.

8:20am **AS+BI+CA+HC+LS+PS+SE+SS-WeM-2 An Electrochemically Polymerized Protective Layer for Magnesium Metal Anode**, *Y. Wang,* University of Maryland College Park*;* ***Alexander Kozen,*** University of Maryland

Rechargeable magnesium (Mg) batteries are promising beyond Li-ion technologies due to their high volumetric capacity (3832 mAh cm^{-3}) and high natural abundance. Nonetheless, Mg metal anode is incompatible with most conventional electrolytes which leads to the formation of an ionically passivating layer. Mg also suffers from growth of dendrites similar to Li, which causes failure of the cells. In this study, we electrochemically polymerized 1,3-dioxolane (DOL) to form a thin Mg^{2+}-conducting elastomeric artificial solid electrolyte interphase (ASEI) layer by electrochemically pretreating Mg metal anodes. We found that this protective ASEI layer enables excellent cyclability of Mg-Mg symmetric cells at high current density (0.5 mAcm^{-2}) over 400 hours at a stable low overpotential (0.50 V vs. Mg^{2+}/Mg) without cell short-circuiting, while untreated pristine Mg symmetric cells quickly failed. The formation of this ASEI also significantly lowered the impedance of the cells, which proved its capability of conducting Mg^{2+} ions. Comprehensive surface chemistry analysis was done by X-ray photoelectron spectroscopy (XPS) which showed that an ASEI mainly consists of poly-DOL was formed, along with various Mg salts which are instrumental to the conductance of Mg^{2+} ions.

More importantly, poly-DOL component in the elastomer was well preserved post-cycling, which contributed to the long-term cyclability and low voltage hysteresis of pretreated Mg-Mg cells, as compared to the pristine ones. Focused ion beam (FIB) – scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) mapping showed that a generally uniform layer was formed on the surface and this ASEI is roughly 200 µm thick and was able to suppress the growth of Mg dendrites after cycling for 400 hours at 0.03 mA cm^{-2} current density, as compared to the rampant sphere-shaped dendrites on the surface of pristine Mg anodes after cycling. This is the first ever report on the successful formation of poly-DOL ASEI on Mg metal anodes as a protective layer and by electrochemical polymerization method that effectively enhanced the electrochemical cycling performance of the Mg metal anodes.

8:40am **AS+BI+CA+HC+LS+PS+SE+SS-WeM-3 Analysis of Surfaces and Interfaces in Polymer Electrolyte Membrane Fuel Cell and Electrolyzer Devices***, **Svitlana Pylypenko**,* Colorado School of Mines **INVITED**

Implementing a hydrogen-based infrastructure depends on developing electrochemical energy conversion devices such as fuel cells and electrolyzers. Polymer electrolyte membrane fuel cells (PEMFCs) have been the focus of research for lightweight renewable transportation applications such as motor vehicles for years, but they also offer the potential to fuel stationary applications, including residential power, due to their potential to produce industrial amounts of energy via a renewable route. Polymer electrolyte membrane water electrolysis (PEMWE) is a promising strategy to produce and store renewable energy in the form of hydrogen for subsequent use in either manufacturing processes, or to run a fuel cell, which can generate electricity on demand.

Great improvements have been made in the development of catalysts and electrodes for PEM systems, improving their activity and stability while reducing the amount of precious metals used. The properties of the electrodes used in these devices are influenced by multiple parameters: the chemical identity of the catalyst and the ionomer; the morphological properties of the catalyst (e.g. shape and surface area); ink formulations; and the various processing parameters used to prepare the electrode. Due to the breadth of possible variable combinations and the inherent complexity of electrode materials, it is unsurprising that PEM electrodes are both morphologically and chemically heterogeneous. Characterization of relevant surfaces and interfaces in these devices, therefore, represents a challenge that requires a multi-technique approach that evaluates all relevant scales and properties and brings a better understanding of the evolution of surfaces and interfaces under more realistic conditions. This talk will discuss the progress towards the comprehensive characterization of the most critical surfaces and interfaces in PEM devices using a combination of X-ray and electron spectroscopy and microscopy methods. Several challenges related to the characterization of catalyst-gas and catalyst-ionomer interactions in these systems will be covered along with results obtained with near-ambient pressure x-ray photoelectron spectroscopy (nAP-XPS). The development of characterization strategies to enable the exploration of a large processing parameter space will be presented, which can then be used to fabricate optimized electrodes with state-of-the-art catalysts as well as electrodes that integrate novel catalysts, all made with scalable routes. And finally, the development of novel approaches toward the characterization of other components of PEM devices such as porous transport layers will also be briefly discussed.

9:20am **AS+BI+CA+HC+LS+PS+SE+SS-WeM-5 XPS Analysis of Battery Materials***, **Sarah Zaccarine**, B. Schmidt, K. Artyushkova,* Physical Electronics USA*; A. Baniya, Q. Qiao,* Syracuse University

Lithium-ion batteries (LIBs) have experienced success including rechargeability and long lifetimes but their limited energy density restricts applications moving forward. Lithium metal batteries (LMBs) offer similar benefits but with much higher achievable energy densities, making them a promising future battery technology. Both LIBs and LMBs are multi-layered, complex systems with many materials and interfaces that each play a critical role in performance and stability. Tuning the composition and morphology of these materials is necessary to create stable, high-performing devices, but the multi-component interfaces, interactions, and dynamic nature of these systems makes characterization challenging. In order to optimize materials properties and improve battery lifetimes, there is a pressing need for physicochemical characterization approaches with high spatial resolution, chemical and morphological analysis, and correlation of synergistic properties. X-ray photoelectron spectroscopy (XPS) is commonly used to characterize the chemical composition of battery materials, and the depth resolution (~10nm) is ideal for analyzing thin layers and interfaces. However, modern XPS instruments have a variety of operating modes and analytical accessories that enable characterization across a variety of lateral and vertical size regimes. Small and large spot comparisons can track overall composition and local features and changes, with scanning microprobe analysis allowing for spatial resolution down to a few microns. X-ray induced secondary electron imaging (SXI), including high-resolution mosaic imaging over a wide sample area, can be used for easy identification of important features and morphological imaging of various battery component materials to complement chemical information. Chemical mapping can visualize distribution of individual elements or chemical species to understand how materials are distributed and change with testing. Additional options address stability concerns associated with Li materials, including a cooling stage to preserve battery chemistry during extended experiment times, where time-resolved profiles are used to compare chemical degradation under controlled temperatures, and incorporating Al Kα and Cr Kα X-rays for non-destructive XPS and hard X-ray photoelectron spectroscopy (HAXPES) analysis of surface (up to ~10nm, Al) and subsurface (up to ~30nm, Cr) composition. Combined, these powerful capabilities enable thorough characterization of battery materials properties for micro- and large-area spectroscopic analysis of surfaces and interfaces and how these properties change under various analytical and operating conditions.

9:40am **AS+BI+CA+HC+LS+PS+SE+SS-WeM-6 Novel Battery Material Analysis with High-Resolution and High-Throughput XPS***, J. Counsell, S. Coultas,* Kratos Analytical Inc., UK*; C. Moffitt,* Kratos Analytical Inc.*; C. Blomfield,* Kratos Analytical Inc., UK*; **Adam Roberts**,* Kratos Analytical Limited, UK

Several material systems will be discussed to give an overview on how XPS can yield information regarding the distribution and chemical speciation of battery materials.

Na-ion batteries are considered to be environmentally favourable alternatives to Li-ion batteries, particularly in the extremely large-scale application of grid storage, given the abundance of Na. However, to date, the battery performance has not been competitive, and promising ternary materials have been plagued by poor stability in air and unsatisfactory long-term cycling. Herein, air/moisture stability is effectively and systematically investigated with XPS, paving the way for material stability to be modified through rational design. Chemical assignments were correlated with performance and oxidation degradation [1]

The significance of sensitivity and detection limit, comparisons of surface and bulk and an approach for pragmatic peak fitting of difficult elemental lines will be discussed along with considerations such as etch artefacts and degradation.

[1] Shipeng Jia *et al*., J. Mater. Chem. A, 2022,10, 251-265

11:00am **AS+BI+CA+HC+LS+PS+SE+SS-WeM-10 Multimodal Analysis and Imaging of the Boehmite Layer on AA6061***, **Lyndi Strange**,* Pacific Northwest National Lab*; X. Yu,* Oak Ridge National Laboratory*; V. Shutthahandan, M. Song, Q. Miller, M. Bowden, J. Gao, Y. Zhang, J. Son, R. Shimskey, R. Prabhakaran,* Pacific Northwest National Lab*; V. Joshi,* Pacific Northwest National Laboratory

Low-enriched uranium (LEU) alloyed with 10% Mo (U-10Mo) is being considered as a promising alternative to oxide-based dispersion fuel with high-enriched uranium for use in research reactors. The configuration of this proposed LEU monolithic fuel plate consists of the U-10Mo plate-type fuel foil with a 25 µm Zr interlayer barrier clad with an aluminum alloy (AA6061). The clad AA6061 is coated with a boehmite layer to prevent corrosion. The boehmite layer has a high pH passivation range, which makes it resistant to oxidation and preferable to protect the Al cladding. Boehmite is usually formed on the AA6061 surface by autoclave processing. Various surface cleaning techniques have been employed such as polishing and etching to clean the surface of the AA6061 prior to boehmite formation. In this study, we examine how pre-treatment of AA6061 using polishing followed by both acid and alkaline etching affects the chemical composition of the boehmite layer using multimodal analysis. Time-of-flight secondary ion mass spectrometry (ToF-SIMS), x-ray photoelectron microscopy (XPS), transmission electron microscopy (TEM), and grazing incidence x-ray diffraction (GI-XRD) were used to understand the changes in the boehmite layer as a result pre-treatment. ToF-SIMS provides a surface sensitive technique to understand the surface composition and characteristics. Spectral similarities were verified using principal comment analysis (PCA). XPS is a complimentary technique that provides quantitative information about the oxidation states present on the surface. Both the SIMS and XPS results suggested oxidation at the surface, which was further investigated using TEM-SAED and GI-XRD. While the GI-XRD results suggested the dominant phase present on the coupon surface is boehmite, TEM-SAED found small amounts of α- and γ-Al_2O_3 present as a result of alkaline etching.

11:20am **AS+BI+CA+HC+LS+PS+SE+SS-WeM-11 Study of $Cs_x(CH_3NH_3)_{1-x}PbBr_3$ Perovskite with XPS Imaging and Small Area Spectra***, **Tatyana Bendikov,*** Weizmann Institute of Science, Israel*; Y. Rakita,* Columbia University*; H. Kaslasi, G. Hodes, D. Cahen,* Weizmann Institute of Science, Israel

Interest in halide perovskite (HaPs) is motivated by the combination of superior optoelectronic properties and ease in synthesizing these materials with a surprisingly low density of electrically active defects.[1] HaPs possess high chemical sensitivity, especially those having an organic cation at their *A* position (*AMX_3*). Although a direct role of the *A* cation in this sensitivity is unclear, and the structural and optoelectronic backbone lie within the *M-X* bond, the type of the *A* cation was shown to impact the chemical stability and, usually indirectly, affect optoelectronic properties of HaPs.[2-3]

X-ray Photoelectron Spectroscopy (XPS), is a surface sensitive technique with a sensitivity that goes down to a single atomic layer, and can provide unique information that relates the elemental composition with the chemical and electronic states of the different elements in the material. Our study focuses on the XPS imaging in combination with selected small area XPS spectra and uses solution-grown, single crystals of mixed *A*-cation $Cs_xMA_{1-x}PbBr_3$(MA = $CH_3NH_3^+$) HaPs as a candidate for investigating heterogeneity within the crystals. With XPS we followed the variations in chemical composition of these crystals. By observing the surface, we found significant changes in the N/Cs ratio, which increases towards the interior of the crystal. Similar variations in N/Cs, but also in Pb/(N+Cs) ratios were found when we studied cross-sections of cleaved crystals. This compositional heterogeneity within the HaPs crystal was not previously reported and was discovered and monitored due to exclusive capabilities of the XPS technique.

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11:40am **AS+BI+CA+HC+LS+PS+SE+SS-WeM-12 Surface Characterization of Mineral Associated Organic Matters in Environmental Samples by Using X-Ray Photoelectron Spectroscopy (XPS)***, **Qian Zhao**, M. Engelhard, O. Qafoku, K. Hofmockel,* Pacific Northwest National Laboratory

Surface characterization is an important analytical approach to understanding the most dynamic interface of a material. The understanding of soil organic matter (SOM) persistence is critical to global carbon (C) cycling. Minerals play an important role in persisting SOM by associating with organic matters (OM) through different interactions. Yet mechanisms of the accumulation of OM in soil are still unclear. Chemical characterization of OM that is associated with minerals provides a mechanistic understanding of mineral-OM interactions. X-ray photoelectron spectroscopy (XPS) analysis allows us to probe the chemical states and speciation of OM on the surface of mineral grains or soil particles. This work used both synthetic mineral-OM complexes and natural soil samples to investigate the chemistry of organics that associate with minerals. In the synthetic system, we adsorbed four organic compounds on a calcite crystal. XPS analysis found the relative concentration of C was higher in OM adsorbed calcite than that in pristine calcite. Further, the deconvolution of C 1s spectra reveals that the calcite surface had a relatively lower abundance of carbonate but a higher abundance of alkanes in the OM adsorbed calcite than pristine calcite, indicating the adsorption of OM on the calcite surface. In the soil system, we incubated agricultural soils with ^{13}C-glucose for 12 months to trace the fate of microbial residues. Size and density fractionation was used to separate mineral-associated organic matter (MAOM) from whole soil. XPS analysis determined C chemistry of necromass on soil particle surfaces by scanning C 1s region of MAOM and non-MAOM fractions. We found that the MAOM fraction had a relatively higher abundance of carbonyl and carboxylic C functional groups and a relatively lower abundance of C-C/C=C group than non-MAOM fraction. It suggests that MAOM fraction is enriched in microbial-derived molecules (i.e., proteins) but has fewer plant detritus (i.e., carbohydrates or lignin) on mineral surfaces. XPS technique allows us to understand the surface chemistry of microbial necromass that is associated with minerals in soil. The chemical speciation information provides us with the potential bonding environment at the interface of minerals and OM.

Chemical Analysis and Imaging Interfaces Focus Topic
Room 302 - Session CA+HC+LS+VT-WeM
Multiphase Interfacial Analysis and Imaging

Moderators: Andrei Kolmakov, National Institute of Standards and Technology (NIST), **Slavomir Nemsak**, Advanced Light Source, Lawrence Berkeley National Laboratory

8:00am **CA+HC+LS+VT-WeM-1 Probing the Impact of Nanoscale Defect Sites in Perovskite Photovoltaic Films with Time-Resolved Photoemission Electron Microscopy***, **Keshav Dani,*** 1919-1 Tancha, Kunigami-kun, Japan **INVITED**

Hybrid perovskite photovoltaic devices have rapidly emerged as promising contenders for next generation, low-cost solar cell technology. Yet, the presence of defect states critically impacts device operation, including device efficiency and potentially long-term stability. Understanding the nature of these defects, and their role in photocarrier trapping, requires techniques that are capable of probing ultrafast photocarrier dynamics at the nanoscale.

In this talk, I will discuss the development of time-resolved photoemission electron microscopy (TR PEEM) techniques in my lab [1, 2], applied to hybrid perovskite solar materials. Thereby, we directly visualize the presence of the performance limiting nanoscale defect clusters and elucidate the role of diffusion in the charge carrier trapping process [3]. By correlating PEEM measurements with other spatially resolved microscopies, we identify different types of defects that form, and study how passivation strategies may have a varied impact on them [4]. Finally, we show that these defect can act as seeds for degradation [5].

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8:40am **CA+HC+LS+VT-WeM-3 Correlating Structure and Chemistry Using Ambient Pressure Photoemission and X-Ray Scattering***, **Slavomir Nemsak**,* Lawrence Berkeley Laboratory Advanced Light Source **INVITED**

In the last two decades, Ambient Pressure X-ray Photoelectron Spectroscopy (APXPS) has established itself as a go-to technique to study heterogeneous and complex materials under reaction environments. Multimodal approaches, which correlate information from two or more complementary techniques, are currently one of the forefronts of the APXPS development [1]. In the past three years, the ALS contributed one such setup: a combined Ambient Pressure PhotoEmission and X-ray Scattering (APPEXS) instrument commissioned and operated at beamline 11.0.2 [2]. The combination of the two in-situ techniques allows correlating structural and chemical information. By using APPEXS, we observed dynamics of the exsolution process of catalyst metallic nanoparticles [3]. To expand the capabilities of APPEXS further, we introduced a new platform using arrays of patterned nanoparticles to study the evolution of catalytic systems under reaction conditions [4]. Future developments of the technique(s) will be also discussed.

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9:20am **CA+HC+LS+VT-WeM-5 Gating of the 2D Hole Transport in Diamond by Subsurface Charges***, E. Strelcov, **Andrei Kolmakov,*** NIST

The unique electronic, physical, and thermal properties of diamond make diamond-based FETs one of the most prospective devices for high-frequency power electronics. Transfer doping of hydrogenated diamond is a common process to form 2D conducting channels in diamond FET. The electron /hole transport of such a device is sensitively dependent on near-surface scatters including charged traps.

Here, using SEM (EBIC) and AFM Kelvin probe force (KPFM) microscopies we report on imaging of the hole transport in narrow conducting channels as a function of the density and depth of near-surface charges. We demonstrate the gating effect induced by trapped charges and discuss the methods to minimize these effects.

9:40am **CA+HC+LS+VT-WeM-6 Development of 0–D Argon Collisional Radiative Model conjoined with Optical Emission Spectroscopy between 1 mTorr to 760 Torr***, **Tag Choi**, N. Abuyazid, D. Patel,* University of Illinois at Urbana-Champaign*; D. Jacobson,* LytEn. Inc*; S. Keniley, S. Dubowsky, D. Barlaz, D. Curreli, D. Ruzic,* University of Illinois at Urbana-Champaign

Optical emission spectroscopy (OES) is a non-invasive plasma diagnostic, which can be utilized with 0-dimensional argon collisional radiative model (Ar CRM) to understand dynamics of excited and charged argon species and determine plasma parameters in the system. This work aims to study rate coefficients of excited and charged argon species, calculate their densities over time and verify the theoretical results with experimental optical spectra in a wide range of pressure regimes. The model considers various types of collisions such as electron and atom excitation/ionization, photon emission, diffusion, penning ionization, and excimer formation. A merit function is used to obtain a better correlation between the theoretical and experimental densities of the various argon species. This allows the model to get a more accurate estimate of the electron temperature and the densities. Various plasma sources are used such as a low pressure inductively coupled plasma (ICP) source, dielectric barrier discharge (DBD), and microwave discharges, to produce different types of plasmas at pressure ranges of 10 – 50 mTorr and 1 – 760 Torr. The optical emission spectra and Langmuir probe measurements are collected for verifications on a low pressure ICP source and DBD discharge. For the verification of atmospheric microwave discharge, OES data is collected for temperature calculations from Specair and the model. Different plasma sources produce different electron temperatures and densities. The ICP source, DBD and microwave discharge have electron temperatures (T_e) of 2 – 5 eV, 1 – 3 eV, and 0.4 – 0.6 eV and electron density (n_e) of 1E16 to 1E18 m^3, 1E18 to 1E21 m^3, and 1E19 to 1E22 m^3 respectively. A methane and argon gas mixture are introduced to the microwave discharge to understand how plasma parameters differ from a pure argon environment.

11:00am **CA+HC+LS+VT-WeM-10 Atomic-Scale Modeling of Bismuth and Argon Clusters Sputtering of Water/Vacuum Interfaces***, **Zbigniew Postawa**, M. Kański, C. Chang, S. Hrabar,* Jagiellonian University, Poland **INVITED**

Modeling of water/vacuum interfaces should consider the high vacuum pressure of water. First, there is continuous evaporation of the liquid into the vacuum chamber, which must be considered. This phenomenon poses a significant challenge for conventional experimental techniques. Yang *et al.* presented a way to reduce the impact of this phenomenon by using a microfluidic channel [1]. This approach uses an ion beam to drill a 2-3 µm window in the channel wall, exposing the liquid flowing below. Such an arrangement allows for maintaining a low base pressure (~10^{-7} mbar) in the measuring chamber. This technique has already been used to study photochemical reactions, biofilms, and liquid-liquid interfaces by secondary ion mass spectrometry or secondary electron microscopy [2]. Recently, another approach minimizing the effect of high vacuum pressure of water that uses a graphene cell encapsulating a liquid was proposed in studies with transmission electron microscopy [3].

Recently, we have developed a new ReaxFF potential parameterization for modeling C/H/O systems designed directly for sputtering simulations [4]. This parametrization is up to 3 times faster than standard ReaxFF. New force-field allowed us to perform molecular dynamics computer simulations of water and graphene-covered water systems sputtered by bismuth and argon clusters. The mechanism of molecular emission from these two systems is investigated. The effect of the projectile size and the influence of the protecting graphene sheet on the emission process is discussed.

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Acknowledgments

The work has been supported by Polish National Science Center Grant 2019/33/B/ST4/01778 and the PLGrid Infrastructure.

11:40am **CA+HC+LS+VT-WeM-12 Finite-Elements Modeling of Solid-Electrolyte Interfaces in Through-Membranes Imaging and in-Liquid Scanning Probe Experiments***, **Alexander Tselev**,* Department of Physics & CICECO-Aveiro Institute of Materials, University of Aveiro, Portugal **INVITED**

Studies of the physicochemical processes at the interfaces between solids and electrolytes interfaces require *operando* multi-parametric measurements with chemical and electric potential sensitivity, in-depth selectivity, as well as with a high lateral resolution. A number of experimental techniques were implemented for this purpose. In this talk, we will describe applications of finite-elements (FE) modeling to elucidate and interpret microscopic imaging and measurements with liquids ranging from non-polar ones to decimole electrolyte solutions. This includes probing through graphene membranes with the use of microscopy and spectroscopy tools based on high-energy beams—X-rays and electron beams, as well as low-energy probing with the use of scanning probe techniques. Scanning probe techniques can be implemented both with probes in liquids and with probes separated from the electrolytes by membranes. We will discuss liquid-solid interface probing by the Kelvin probe force microscopy (KPFM) through graphene membranes as well as by near-field microwave microscopy through dielectric membranes. Furthermore, models for piezoresponse force microscopy and KPFM with probes immersed in electrolytes will be presented. Support of this work by the project CICECO-Aveiro Institute of Materials, financed by national funds through the FCT/MEC (Portugal) and when appropriate co-financed by FEDER under the PT2020 Partnership Agreement is acknowledged.

Fundamental Discoveries in Heterogeneous Catalysis Focus Topic

Room 321 - Session HC+AS+SS-WeM

Advances in Materials and Analysis in Heterogeneous Catalysis II

Moderators: Sanjaya Sennayake, Brookhaven National Laboratory, **Jason Weaver**, University of Florida

8:20am **HC+AS+SS-WeM-2 Development and Characterization of Highly Stable ALD Coated Catalysts for Dehydrogenation of Light Alkanes***, **Jonathan Travis**, J. Burger, A. Dameron,* Forge Nano

Catalysts are critical materials for enabling many modern industrial chemical processes, such as the dehydrogenation of light alkanes to produce “on purpose” alkenes. Catalyst deactivation costs the chemical industry billions of dollars. One of the major mechanisms of deactivation is metal sintering during high temperature regeneration. Atomic Layer Deposition (ALD) overcoating has previously been demonstrated to stabilize catalyst materials against sintering and deactivation, as well as improve selectivity in certain cases. In this study the properties and performance of 0.1% Pt/Al_2O_3 catalysts are investigated as a function of surface modification via ALD Al_2O_3 coatings. The catalysts are characterized in Forge Nano’s in-house catalyst characterization laboratory. Physical characterization is performed using various techniques including moisture analysis, BET Surface Area, Porosimetry, TGA, CO Chemisorption, ICP-MS, and Temperature Programmed Reduction, Desorption, and Oxidation. Performance is characterized using propane dehydrogenation under a variety of conditions. This talk will present the effects of Forge Nano’s ALD

Al_2O_3 coating on the properties and performance of the 0.1% Pt/Al_2O_3 catalysts.

8:40am **HC+AS+SS-WeM-3 Combining Theory with Ambient Pressure XPS to Reveal Chemistry at Interfaces Under *In Situ* and *Operando* Conditions*,* *Ethan Crumlin,*** Lawrence Berkeley National Laboratory **INVITED**

Interfaces play an essential role in nearly all aspects of life and are critical for electrochemistry. Electrochemical systems ranging from high-temperature solid oxide fuel cells (SOFC) to batteries to capacitors have a wide range of essential interfaces between solids, liquids, and gases which play a pivotal role in how energy is stored, transferred, and converted. This talk will focus on using ambient pressure XPS (APXPS) to directly probe the solid/gas and solid/liquid electrochemical interface. APXPS is a photon-in/electron-out process that can provide both atomic concentration and chemical-specific information at pressures greater than 20 Torr. Using synchrotron X-rays at Lawrence Berkeley Nation Laboratory, the Advanced Light Source has several beamlines dedicated to APXPS endstations that are outfitted with various *in situ*/*operando* features such as heating to temperatures > 500 °C, pressures greater than 20 Torr to support solid/liquid experiments and electrical leads to support applying electrical potentials support the ability to collect XPS data of actual electrochemical devices while it's operating in near ambient pressures. This talk will share our efforts to combine theory and APXPS to understand the chemistry at solid/gas and solid/liquid interfaces under *in situ* and *operando* conditions. At the solid/gas interface, we will share our work to understand how carbon dioxide interacts with copper and silver surfaces using APXPS and theory to generate observables that we could experimentally verify. Separately I will introduce our strategy to introduce a chemical reaction network to generate spectra of water interacting with a silver surface that directly resembled our APXPS measurements. At the solid/liquid interface, the combination of theory and APXPS revealed how stable magnesium electrodes and stable diglyme electrolytes could be unstable when in contact with each other. In addition, it facilitated the prediction of the sensitivity for probing interfacial chemical species at a solid/liquid interface. To further advance these directions and synergy for combining theory and experiments, I will show our recent progress in creating an interfacial Digital Twin that we hope will rapidly accelerate our understanding of interfacial chemistry.

9:20am **HC+AS+SS-WeM-5 The Electrochemical Interface as a Reactive Environment to Resynthesize Electrode Surface Chemistry Using the Dissolution-Redeposition Dynamics*, Feng Lin,*** Virginia Tech **INVITED**

The solid-liquid electrochemical interface offers a two-dimensional environment for geometrically confined interfacial reactions to tailor electrode surface chemistry under operating conditions. Herein, we demonstrate that the dissolution and redeposition kinetics of transition metal cations, a ubiquitous phenomenon at the electrochemical interface, can be manipulated to regulate the chemical composition and crystal structure of the electrode surface as well as the overall electrochemical performance. Foreign cations, either added as electrolyte additives or dissolved from surface coatings, can rapidly participate in the electrode dissolution-redeposition process, and facilitate the establishment of the dissolution-redeposition equilibrium. We will present scientific case studies in electrocatalysis. Our work expands the control over the electrochemical reactions at the solid-liquid interface and provides new insights into interfacial studies in electrochemistry, and surface science.

11:00am **HC+AS+SS-WeM-10 Ambient Pressure Spectroscopy of Catalytic Porous Nanofilms***, C. Eads,* MAX IV Laboratory, Sweden*; T. Hu, S. Tenney,* ***Ashley Head,*** Brookhaven National Laboratory **INVITED**

Porous materials offer an opportunity for catalysis in confined spaces. By spatially confining chemistry, reaction dynamics and selectivity can change in unknown ways. Two examples will be discussed, including Pt nanoparticles embedded in a thin film of the metal-organic framework UiO-66(NH_2) and a two-dimensional silicate on Pd(111). Ambient pressure X-ray photoelectron spectroscopy (APXPS) has been used to characterize the electronic structure of the Pt-embedded metal-organic framework. CO oxidation and CO_2 reduction have been followed with IR spectroscopy and mass spectrometry. In a second system, the space between a two-dimensional silicate and a Pd(111) surface promotes more CO oxidation than a bare Pd surface. IR spectroscopy shows that the silicate film changes the surface adsorbates, resulting in increased CO_2 formation, as confirmed with mass spectrometry. These results will help enable the rational design of materials to spatially confine reactions in a desired way.

11:40am **HC+AS+SS-WeM-12 Catalytic Oxidation of Methane on IrO_2(110) Films*, Jovenal Jamir,*** *R. Martin,* University of Florida*; M. Kim,* Yeungnam University , Republic of Korea*; C. Lee, V. Mehar,* University of Florida*; A. Asthagiri,* The Ohio State University*; J. Weaver,* University of Florida

In recent years, IrO_2(110) films have gained increasing interest for their ability to strongly adsorb light alkanes and cleave C-H bonds below room temperature. Our group has shown, via ultrahigh vacuum (UHV) temperature programmed reaction spectroscopy (TPRS) experiments, that initial methane activation occurs at temperatures as low as 100 K and leads to the desorption of CO, CO_2 and H_2O above 400 K. The large temperature range over which partially oxidized methane-derived species exist, along with the facile nature of C-H bond cleavage motivates further study of methane oxidation under catalytically relevant conditions. In this talk I will discuss recent kinetic studies performed in a batch reactor to investigate the catalytic oxidation of CH_4 on IrO_2(110) films at gas pressures near 1 Torr as well as results of ambient pressure x-ray photoelectron spectroscopy (AP-XPS) measurements and molecular simulations. We find that IrO_2(110) is highly active for the catalytic combustion of CH_4 at moderate temperatures (500-650 K), with comparable activities to PdO catalysts. Our results further show that catalytic CH_4 oxidation is mildly activated on IrO_2(110) and that the catalytic rates depend slightly inversely on the O_2 partial pressure, suggesting that the dissociative chemisorption of O_2 is more efficient than CH_4 activation and acts to blocks CH_4 adsorption sites. AP-XPS measurements reveal that high coverages of OH groups and CH_yO_2 species form on IrO_2(110) during CH_4 oxidation and that O-rich IrO_2(110) surfaces are maintained even under highly CH_4-rich conditions (up to 95% CH_4), consistent with efficient O_2 adsorption and site competition with CH_4. Finally, I will discuss how we have combined our AP-XPS results with catalytic rate measurements to develop first principles, microkinetic models for methane oxidation over IrO_2(110). Of particular significance is that earlier models did not consider surface CH_yO_2 species. Our AP-XPS results thus inspired efforts to identify additional reactions and determine the roles that various adsorbed species play during catalytic CH_4 oxidation on IrO_2(110). Our findings highlight how operando surface spectroscopy can provide key guidance for understanding catalytic reaction mechanisms and developing accurate kinetic models.

12:00pm **HC+AS+SS-WeM-13 HC Graduate Student Finalist Talk: *Operando* Observation of Metal Encapsulation Causing Strong Metal-Support Interaction at the Pt-Co_3O_4 Interface*, Daeho Kim,*** Korea Advanced Institute of Science and Technology (KAIST) & Institute for Basic Science (IBS), Republic of Korea*; D. Park,* Korea Advanced Institute of Science and Technology, Republic of Korea*; H. Song,* Korea Advanced Institute of Science and Technology (KAIST) & Institute for Basic Science (IBS), Republic of Korea*; B. Jeong,* Korea Basic Science Institute (KBSI), Republic of Korea*; Y. Jung,* Korea Advanced Institute of Science and Technology, Republic of Korea*; J. Park,* Korea Advanced Institute of Science and Technology (KAIST) & Institute for Basic Science (IBS), Republic of Korea

Noble metal nanoparticles (NPs) supported on metal oxide (e.g., Co_3O_4, NiO, TiO_2, CeO_2, and Fe_2O_3) have been commonly utilized as a heterogeneous catalyst for improving catalytic performance and modifying the reaction pathway of various catalytic reactions, such as CO oxidation, CO_2 hydrogenation, and Fischer-Tropsch synthesis. The unique interaction at the interface of the metal NP and oxide, which is known as the strong metal-support interaction (SMSI), gives synergistic enhancement to the catalytic activity. Hence, a fundamental understanding of SMSI with bridging pressure and material gaps using operando surface characterization is necessary for developing high-performance heterogeneous catalysts.

Herein, we show the direct evidence of SMSI at the interface of Pt NP and Co_3O_4, utilizing operando surface analysis. The Pt-Co_3O_4 interfaces were prepared as powder catalysts using colloidal Pt NPs embedded on the mesoporous Co_3O_4. The two-dimensional model system is also constructed on Co_3O_4–coated Si wafer via a Langmuir-Blodgett trough to bridge the material gap. The surface of prepared Pt-Co_3O_4 is comprehensively characterized under dynamic conditions: a reducing environment (H_2 or CO) and a catalytic reaction environment (CO + O_2). Combining computational calculation and the operando surface characterizations using ambient pressure X-ray photoelectron spectroscopy, environmental transmission electron microscopy, and diffuse reflectance infrared Fourier-transform spectroscopy, we suggest that the interface between Pt NPs and the thin oxide overlayer is a key state of the SMSI enhancing the catalytic activity.

Magnetic Interfaces and Nanostructures Division
Room 330 - Session MI-WeM

Spin Landscape I (Magnetic Structures in Real and Momentum Space)

Moderator: Mikel Holcomb, West Virginia University

8:00am **MI-WeM-1 Voltage Controlled Néel Vector Rotation in Zero Magnetic Field**, ***Christian Binek**, A. Mahmood,* University of Nebraska-Lincoln; *W. Echtenkamp,* University of Minnesota; *M. Street, J. Wang, S. Cao, T. Komesu, P. Dowben, P. Buragohain, H. Lu, A. Gruverman, A. Parthasaraty, S. Rakheja,* University of Nebraska-Lincoln; *J. Weaver, J. Lynn,* NIST-Gaithersburg **INVITED**

Voltage-controlled switching of remnant magnetic states paves the way towards ultra-low power and non-volatile spintronics. In this presentation, I report on a decade-long journey which took us from isothermal electric switching of exchange bias with the help of simultaneously applied electric and magnetic fields to pure voltage-controlled antiferromagnetic spintronics in zero magnetic field and at CMOS compatible temperatures. Nonvolatile Néel vector reorientation in the absence of an applied magnetic field, *H*, is demonstrated at CMOS compatible temperatures in prototype device structures which exploit the multi-functional properties of thin films of boron (B) doped Cr_2O_3. Boundary magnetization associated with the Néel vector orientation serves as state variable which is read via magnetoresistive detection in a Pt Hall bar adjacent to the B: Cr_2O_3 film. Switching of the Hall voltage between zero and non-zero values implies Néel vector rotation by 90-degrees in agreement with the observed voltage dependent contrast in magnetic force microscopy images. Piezo force microscopy data suggest the presence of polar nanoregions which give rise to uniform polarization in the presence of an applied electric field. The polarization is accompanied piezoelectric straining which, via magnetoelastic coupling, changes the magnetic anisotropy and thus the Néel vector orientation from out of plane to in-plane and back. B-doping enhances the Néel temperature, T_N, of pure chromia. Annealing of the device further increases the T_N-enhancement (up to 500K) at the interface between the Hall bar and the B: Cr_2O_3 surface via thermally activated B-diffusion. The diffusion mechanism is confirmed via cold neutron depth profiling measurements. Robust switching is demonstrated post-annealing for temperature as high as 400K. Theoretical modeling estimates switching speeds of about 100 ps making B: Cr_2O_3 a promising multifunctional single-phase material for energy efficient nonvolatile CMOS compatible memory applications.

We acknowledge financial support by NSF/EPSCoR RII Track-1: Emergent Quantum Materials and Technologies, OIA-2044049. The research was performed in part in the NNF: NNCI and the NCMN, supported by NSF under ECCS:2025208, and the NRI.

8:40am **MI-WeM-3 Discovering Magnetic Mechanisms in Room-Temperature Metallic Antiferromagnet Fe_3Ga_4**, ***Michelle Jamer**, B. Wilfong,* United States Naval Academy; *D. Baigutlin, O. Miroshkina, V. Buchelnikov, V. Sokolovskiy,* Chelyabinsk State University, Russian Federation; *G. Stephen, A. Friedman,* Laboratory for Physical Sciences; *R. Barua,* Virginia Commonwealth University; *B. Barbiellini,* LUT University, Finland; *D. Heiman,* Northeastern University **INVITED**

Recently, Fe_3Ga_4 has garnered much interest due to its unique magnetic structure which supports two unique magnetic transitions- one metamagnetic transition at low temperature to an antiferromagnetic helical spin structure (~70 K), and a second transition between the antiferromagnetic state to ferromagnetic state (~360 K). Due to the helical spin structure of the intermediate antiferromagnetic state, metallicity is not prohibited leading to the possibility of a room temperature metallic antiferromagnet, which is attractive for potential spintronic devices. Of particular interest, is fully understanding the magnetic phase diagram and the Fe-Fe coupling in the lattice which gives rise to the special helical ordering. In our work, we have prepared bulk ingots and single crystals of this compound to understand the magnetic coupling of Fe_3Ga_4 to determine the baseline properties. Through adding pressure to the system, we have found that we are able to change the transition temperatures of the magnetic states- leading to an increase in the low temperature transition and a decrease in the high temperature transition. In these measurements, we have found that we are able to tune the high temperature transition to room temperature by adding pressure -while the structure retains its metallicity. A full discussion on the baseline Fe_3Ga_4 as well as its changes with pressure will be presented, including theoretical calculations supporting the magnetic structure as detected via magnetometry measurements.

11:00am **MI-WeM-10 Irradiative Control of FeRh's Metamagnetic Phase Change Under Three-Dimensional Spatial Confinement Interrogated by Polarized Neutron Scattering**, ***Steven Bennett**,* Naval Research Laboratory **INVITED**

Phase change materials have been a staple for a wide array of memory technologies for many decades. The promise of antiferromagnetic electronics has pushed the envelope past using a straight forward resistive phase change, to the realm of high speed spin flipping, incommensurate spin density waves and magnonics which can propagate without a local magnetic anisotropy to hinder spin rotation. In this new memory paradigm we will need to develop a new set of materials and understanding of spin physics from which to build this next generation of high speed and low energy loss devices. In this seminar I will provide an overview of my teams recent discoveries on how the metamagnetic transition in FeRh, from antiferromagnetic to ferromagnetic ordering, can be controlled and triggered using low energy heavy and light ion irradiation [1][2], as well as joule heating in confined wire device geometries at high switching speeds. We interrogate the complexities of these spin systems using polarized neutron scattering, revealing highly localized effects of ion irradiation in the films and uncover a new effect for metamagnetic spin dynamics which could be pivotally important for modern antiferromagnetic spintronics.

[1] S.P. Bennett et. Al., Coatings, 11(6), 661, (2021)

[2] C. D. Cress et. Al., ACS Appl. Mater. Interfaces 13, 1, 836–847, (2021)

Nanoscale Science and Technology Division
Room 304 - Session NS+AP+BI+SS-WeM

Frontiers in Scanning Probe Microscopy Including Machine Learning

Moderators: Wonhee Ko, University of Tennessee, Knoxville, **Adina Luican-Mayer**, University of Ottawa, Canada

8:40am **NS+AP+BI+SS-WeM-3 Decay Rate Spectroscopy for a Direct Probe of Josephson and Andreev Currents on the Atomic Scale**, ***Wonhee Ko**,* University of Tennessee, Knoxville; *J. Lado,* Aalto University, Finland; *E. Dumitrescu, P. Maksymovych,* Oak Ridge National Laboratory

The tunneling current in superconducting tunnel junctions involves several mechanisms in addition to the normal-electron tunneling, such as Josephson tunneling and Andreev reflection. Identification of the tunneling mechanisms as a function of external parameters, such as barrier height, bias voltage, temperature, and so on, is the key to elucidating the characteristics of the superconductors, such as paring symmetry and topology. Here, we present a method to identify distinct tunneling modes based on the decay rate of tunneling current measured by scanning tunneling microscopy (STM) [1,2]. Precise control of the tip-sample distance in picometer resolution allows us to quantify the decay rate as a function of bias *V* and tip height *z*, with which we identified the crossover of tunneling modes between single-charge quasiparticle tunneling, (multiple) Andreev reflection, and Josephson tunneling. The method was both applied to S-I-S [1] and S-I-N [2] junctions, to unambiguously identify Josephson and Andreev currents. Moreover, mapping decay rates in the atomic resolution with STM revealed the intrinsic modulation of Andreev reflection and Josephson current. The result shows that the decay rate spectroscopy will be crucial for addressing the superconducting characteristics of the materials and their applicability for Josephson-junction devices.

This research was performed at the Center for Nanophase Materials Sciences which is a DOE Office of Science User Facility.

[1] W. Ko, E. Dumitrescu, and P. Maksymovych, *Phys. Rev. Res.***3** 033248 (2021)

[2] W. Ko, J. L. Lado, and P. Maksymovych, *Nano Lett.***22** 4042 (2022)

9:00am **NS+AP+BI+SS-WeM-4 Machine Learning-Driven Automated Scanning Probe Microscopy: Application to Ferroelectric Materials***, **Yongtao Liu**, K. Kelley, R. Vasudevan,* Oak Ridge National Laboratory, USA*; H. Funakubo,* Tokyo Institute of Technology, Japan*; S. Kalinin,* University of Tennessee Knoxville*; M. Ziatdinov,* Oak Ridge National Laboratory, USA

Scanning probe microscopy (SPM) has become a mainstay of many scientific fields including materials science, condensed matter physics, and so on. Machine learning (ML) and artificial intelligence (AI) have been applied to determine the physical mechanisms involved in phenomena encoded within microscopy data, enabling ML/AI to rapidly become an indispensable part of physics research. However, the real-time connection between ML and microscopy—which enables automated and autonomous experiments for microscopy imaging and spectroscopy measurements—still lags. Until now, the search for interesting functionalities in microscopy experiments has been guided by auxiliary information from microscopy to identify potential objects of interest based on human intuition; the exploration and verification of physical mechanisms depend on human-based decision making, i.e., operators determine the parameters for subsequent experiments according to the previous experiment. Here, we developed ML-driven automated experiment (AE) scanning probe microscopy (SPM) workflow to learn the functionality and mechanism in materials in an automatic manner. We demonstrate the application of deep kernel learning and hypothesis learning based workflows by investigating ferroelectric materials, including studies of domain wall dynamics, domain switching mechanism, the conductivity of topological defects, and relationship between domain structure and local properties. Using these approaches, we observe larger hysteresis opening near 180^{o} domain walls due to the larger polarization mobility in the vicinity of the 180^{o} walls in a $PbTiO_3$ sample and find that the domain switching in a $BaTiO_3$ thin film is determined by the kinetics of the domain wall motion, etc. We implemented these approaches in SPM for ferroelectric materials investigation, however, the workflows are universal and can apply to a broad range of imaging and spectroscopy methods, e.g., electron microscopy, optical microscopy, and chemical imaging.

Acknowledgements: This work (implementation, measurement, and data analysis) was primarily supported by the center for 3D Ferroelectric Microelectronics (3DFeM), an Energy Frontier Research Center funded by the U.S. Department of Energy (DOE), Office of Science, Basic Energy Sciences under Award Number DE-SC0021118. This work (ML development) was supported by the Center for Nanophase Materials Sciences, a US Department of Energy Office of Science User Facility.

9:20am **NS+AP+BI+SS-WeM-5 AVS Dorothy M. and Earl S. Hoffman Scholarship Talk: Direct Imaging of Light-Matter Interaction of 0-dimensional Excitonic Emitters using Tip-enhanced Scanning Probe Technique***, **Kiyoung Jo**[1], E. Marino, J. Lynch, Z. Jiang, N. Gogotsi,* University of Pennsylvania*; P. Schuck,* Columbia University*; N. Borys,* Montana State University*; C. Murray, D. Jariwala,* University of Pennsylvania

Strong light-matter interactions of 0-dimensional emitters on plasmonic Au substrate were explored using both contact and tapping mode tip-enhanced scanning probe micro-spectroscopy. The plasmonic tip engaged with contact mode couples with the excitonic dipole in CdSe-CdS nanoplatelets, leading to strong exciton-plasmon coupling. Unlike the contact mode, the directional propagation of surface plasmon polariton from the excitonic emission of the nanoplatelets on Au as wave-like fringe patterns was probed by taking advantage of the tapping mode. Since tapping mode operates a few nanometers away from the surface, the near-field photoluminescence with in-plane wavevectors can be collected, leading to form fringe patterns propagating from the quantum plate. Extensive optical simulations proved that the fringes are the result of standing wave formed between the tip and the nanoplatelets. The effect of excitonic dipole orientation and dielectric layers on the fringe patterns were investigated by the simulation which matched with experimental results. The fringe patterns were also observed in WSe2 nano-bubbles, and the CdSe/CdS nanoplatelet in SiO2/Si substrate which means the phenomenon is universal in 0-dimensional emitters and various substrates. We envision that the discovery excels in understanding in-plane near-field light signal transduction from 0-dimensional emitters toward nano and quantum photonics.

9:40am **NS+AP+BI+SS-WeM-6 Nanoscale Subsurface Depth Sensitivity of Contact Resonance Atomic Force Microscopy on Layered Films***, **Gheorghe Stan**,* National Institute for Science and Technology (NIST)*; C. Ciobanu,* Colorado School of Mines*; S. King,* Intel Corporation

Probing the mechanical properties is one of the basic inquiries that can reveal the structure and integrity of an isolated material or multicomponent system. At the nanoscale, due to size constrains and defects, mechanical tests become even more relevant as the properties of a part may differ by those of the whole. Over years, contact resonance AFM (CR-AFM) has proved to be a reliable AFM-based technique for nanoscale mechanical property measurements. Mostly operated into the elastic modulus range from few GPa to hundreds of GPa, CR-AFM was used to test different materials and structures at the nanoscale and considered for discerning the mechanical response of subsurface inhomogeneities and buried domains. It remains, however, to directly prove the extent of its quantitative capabilities both in terms of elastic modulus and depth sensitivity. In this work, we develop a quantitative methodology to test the elastic modulus and depth sensitivity of CR-AFM against a set of low-k dielectric bilayer films with the top layer of various thicknesses. We have analyzed the measured contact stiffness as a function of load and film thickness with both a semi-analytical model and three-dimensional finite element analysis. Both analyses confirmed the expected elastic moduli of the layered structures and provided a robust quantitative estimation of the subsurface depth and material sensitivities of CR-AFM. We also developed a correlative measurement-model analysis to assess the convoluted contributions of the structural morphology and mechanical properties to the contact stiffness used by AFM-based subsurface imaging. The results explain the inherent difficulties associated with solving concurrently the material contrast and location of subsurface heterogeneities in nanomechanical subsurface imaging.

11:00am **NS+AP+BI+SS-WeM-10 The Impact of Temperature on Viscoelastic Properties of Nanoscale Domains Within Polymer Composites***, **Bede Pittenger**, S. Osechinskiy, J. Thornton, S. Loire, T. Mueller,* Bruker Nano Surfaces

The behavior of polymer composites is controlled by the properties of the components as well as the microstructure of the material. Because confinement effects and interphase formation can alter properties of the microphases, only measurements performed directly on the composite can provide the needed local property distribution. Mechanical properties of polymers are generally temperature (and time) dependent, so a full understanding requires measurements over a range of temperatures and frequencies. Ideally, one would like to observe the mechanical behavior of these microscopic domains while they pass through their glass transitions to appreciate the influence of size effects and confinement on time dependent mechanical properties.

Recently, Atomic Force Microscopy based nano-Dynamic Mechanical Analysis (AFM-nDMA) was introduced. Like bulk DMA, this mode provides spectra of storage and loss modulus across frequency and temperature, allowing construction of master curves through Time Temperature Superposition (TTS). In addition, it allows high resolution measurements localized to the microscopic structures within heterogeneous samples. This presentation will examine the capabilities of this new mode with examples in a wide range of polymers and composites.

11:20am **NS+AP+BI+SS-WeM-11 AFM Force Spectroscopy Combined with Machine-Learning Methods for Identifying Malaria Derived- EV Subpopulations***, **Irit Rosenhek-Goldian**, P. Abou Karam,* Weizmann Institute of Science, Israel*; T. Ziv,* Technion - Israel Institute of Technology, Israel*; H. Ben Ami Pilo, I. Azuri, A. Rivkin, E. Kiper, R. Rotkopf, S. Cohen,* Weizmann Institute of Science, Israel*; A. Torrecilhas,* Federal University of São Paulo, Brazil*; O. Avinoam,* Weizmann Institute of Science, Israel*; A. Rojas,* University of Costa Rica*; M. Morandi, N. Regev-Rudzki,* Weizmann Institute of Science, Israel

The Malaria (*Plasmodium falciparum*) parasite releases extracellular vesicles (EVs) which modulate the mechanical properties of the host red blood celland thus facilitate parasite action. It is understood that EVs are composed of sub-populations with different functions, but little is known of their nature and specialized function. Here, we report the use of Atomic Force Microscopy (AFM) imaging and puncture analysis, combined with state-of-the-art size separation techniques and several biochemical, microscopic and spectroscopic characterization techniques in an attempt to differentiate and characterize the different populations. Specifically, we subjected malaria-derived EVs to size-separation analysis, using Asymmetric Flow Field-Flow Fractionation (AF4). The fractions obtained

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[1] **AVS Dorothy M. and Earl S. Hoffman Scholarship Recipient**

were characterized by Cryo-transmission electron microscopy (cryo-TEM), and AFM which revealed the presence of two distinct EV subpopulations - small (10-70 nm) and large (30-500 nm). Proteomic analysis revealed that the small EVs were enriched in complement-system proteins and the large EVs with proteasome subunits. In addition, Förster resonance energy transfer (FRET)-based fusion assay showed that small EVs fused to early-endosome liposomes at significantly greater levels than large EVs. Finally, AFM puncture analysis characterized by unsupervised machine-learning verified the presence of two distinct fractions with respect to mechanical behavior which correlate with the EV size groupings. These results shed light on the sophisticated mechanism by which malaria parasites utilize EV subpopulations as a communication tool to target different cellular destinations or host systems.

Plasma Science and Technology Division
Room 305 - Session PS1+AP+TF-WeM

Plasma Deposition and ALD Processes for Coatings and Thin Films

Moderators: Sumit Agarwal, Colorado School of Mines, **Adriana Creatore**, Eindhoven University of Technology, Netherlands

8:00am **PS1+AP+TF-WeM-1 Hollow Cathode Enhanced Capacitively Coupled Plasmas in Ar / N_2 / H_2 Mixtures and Implications for Plasma Enhanced ALD***, **David Boris**,* U.S. Naval Research Laboratory*; M. Johnson,* Syntek Technologies*; C. Eddy,* ONR Global*; S. Walton,* U.S. Naval Research Laboratory

Plasma enhanced atomic layer deposition (PEALD) is a cyclic atomic layer deposition (ALD) process that incorporates plasma-generated species into one of the cycle sub-steps. The addition of plasma is advantageous as it generally provides unique gas-phase chemistries and a substantially reduced growth temperature compared to thermal approaches. However, the inclusion of plasma, coupled with the increasing variety of plasma sources used in PEALD, can make these systems challenging to understand and control. This work focuses on the use of plasma diagnostics to examine the plasma characteristics of a hollow cathode enhanced capacitively coupled (HC-CCP) plasma source, a type of plasma source that has seen increasing attention in recent years for PEALD. Ultraviolet to near-infrared (UV-NIR) spectroscopy as well as spatially resolved Langmuir probe and emissive probe measurements are employed to characterize an HC-CCP plasma source using nitrogen based gas chemistries typical of nitride PEALD processes. Spectroscopy is used to characterize the relative concentrations of important reactive and energetic neutral species generated in HC-CCP systems as a function of applied RF power, gas chemistry and pressure. In addition, the electron energy distribution function, electron temperature, plasma potential, and plasma density for the same process parameters are examined using an RF compensated Langmuir probe and emissive probe.These measurements indicated that electron temperature (T_e), electron density (n_e), and plasma potential (V_p) varied significantly over the operating conditions examined with Te varying from 1.5 to 8 eV, Vp varying from 30V to 90V, and ne varying between 10^{15} m-3 and low 10^{16} m-3.This wide range plasma conditions is mediated by a mode transition from a low T_e, high ne mode of operation at low pressure (<100 mTorr) to a high T_e, low n_e mode at higher pressures (>100 mTorr).These operational modes appear analogous to the classical γ and α modes of traditional capacitively coupled plasmas.Atomic N and H densities also vary significantly over the operating conditions examined.

8:20am **PS1+AP+TF-WeM-2 Chasing Oxygen Out of Nitrides Grown on PEALD and Thermal ALD***, **Bangzhi Liu**,* The Pennsylvania State University*; B. Rayner,* KJ Lesker

It is not uncommon to see O content above 10% inside nitrides grown on both thermal and plasma ALD reactors. One typical example is TiN. Ti is extremely reactive and will combine with any O present inside the reactor. It has been reported that O can come from multiple sources [1], including o-ring seals, impurities inside UHP gases (Ar and N2), plasma tube, etc. By adding differential pumping to gate valve seal, chamber seal, and plasma tube seal on our Lesker 150LX system, and purifying Ar and N2 gases, the O level is reduced below 1% inside TiN film. By correlating TiN growth per cycle, ellipsometry thickness uniformity mapping, and sheet resistance to O level measured by XPS, we can monitor O level inside the reactor precisely and verify the ultra-high purity (UHP) condition of the chamber. By maintaining UHP condition, extreme high purity AlN and BN have been prepared. Surprisingly, extremely low-level O (barely detectable by XPS) was found inside ZrN prepared on our thermal ALD reactor, Lesker 150LE due to a special design of the chamber. This opens a door to high purity nitrides on thermal ALD reactor. In this talk, experimental data will be presented to show the interaction between O level inside ALD nitrides and system design.Practical engineering controls enabling UHP nitrides will be discussed.

[1] Ultrahigh purity conditions for nitride growth with low oxygen content by plasma enhanced atomic layer deposition, J. Vac. Sci. Technol. A 38, 062408 (2020); Gilbert B. Rayner, Noel O'Toole, Jeffrey Shallenberger, et al.

8:40am **PS1+AP+TF-WeM-3 Area-Selective Deposition: A Bottom-Up Approach to Nanoelectronics Fabrication***, **Silvia Armini**,* IMEC, Belgium **INVITED**

Area-selective deposition (ASD)-driven processes recently gained a lot of attention from the microelectronics industry as a potential solution for the issues associated with top-down pattern formation at the nanoscale.

The first part of this talk is focused on the ASD of TiO_2 and Ru deposited by atomic layer deposition (ALD). In this respect, as an ALD inhibition route, we have been investigating both hydrogen and halogen plasma surface modification of amorphous carbon materials (non-growth area) and methyl-terminated monomolecular organic films on SiO_2 (non-growth area) substrates. On one side, on a-C non-growth area, we examined the possibility of combining two defect-reduction strategies by employing low power Cl_2 or CF_4 plasmas for both surface functionalization/re-functionalization and for removal of nuclei.

The second part of this talk is focused on selective metal passivation films for Dielectric on Dielectric deposition. We review our current understanding of the relationship between structure and properties of the inhibiting materials and the correspondent surface dependence of different ALD processes. Nucleation and growth behaviour of ALD on different surfaces functionalized by organic films will be analyzed, such as the interaction between ALD conditions (i.e. temperature, coreactants...) and the extent of decomposition and modification of the organic films.

9:20am **PS1+AP+TF-WeM-5 The Role of Plasma in Plasma Enhanced Atomic Layer Epitaxy***, **Scott Walton**, D. Boris,* US Naval Research Laboratory*; M. Johnson,* Syntek Technologies, Inc.*; V. Wheeler, J. Woodward, S. Rosenberg, S. Johnson,* US Naval Research Laboratory*; K. Ludwig,* Boston University*; J. Hite, C. Eddy,* US Naval Research Laboratory

Plasma-enhanced atomic layer deposition (PE-ALD) is a low temperature, conformal, layer-by-layer deposition technique that is based on a pair of self-terminating and self-limiting gas-surface half-reactions, in which at least one half-reaction involves species from a plasma.This approach generally offers the benefit of substantially reduced growth temperatures and greater flexibility in tailoring the gas-phase chemistry to produce films of varying characteristics and has been successfully employed to grow epitaxial films.The plasma-based advantages come at the cost of a complex array of process variables that can drastically impact the resulting film properties.We employ plasma diagnostics to inform the choice of process conditions for PE-ALD systems including VUV-NIR spectroscopy, charged particle collectors near the substrate, and spatially resolved Langmuir probe measurements to characterize the plasma used in commercial and research PE-ALD tools.In particular, we assess the total ion flux reaching the substrate surface, spatial variation of plasma properties, and the relative fractions of atomic and molecular species generated in the plasma under a variety of pressures and gas input flow fractions typically used to grow epitaxial nitride and oxide films. Changes in plasma parameters are then linked with changes in growth modes and characteristics of films including AlN, InN, TiO_2 and Ga_2O_3. This work is partially supported by the Office of Naval Research and the Naval Research Laboratory base program.

9:40am **PS1+AP+TF-WeM-6 Plasma-Enhanced Atomic Layer Deposition of TiAlN Thin Films: A Novel Approach for MAX-phase Synthesis***, **Moses Nnaji**,* Georgia Institute of Technology, USA*; D. Hitchcock,* Savannah River National Laboratory, USA*; E. Vogel,* Georgia Institute of Technology, USA

MAX-phases are a class of layered hexagonal carbides and nitrides that possess a hybrid metal-ceramic character with a desirable combination of mechanical properties.[1] Consequently, many MAX-phase coatings are attractive for applications requiring extreme heat and corrosion resistance. However, conventional synthesis of MAX-phases such as $Ti_{n+1}AlX_n$ requires high-temperatures (800-1000 °C), limiting applications for temperature-sensitive materials.[2] Plasma-enhanced atomic layer deposition (PEALD), however, may be capable of MAX-phase $Ti_{n+1}AlX_n$ synthesis at low temperatures (<600 °C) since it (1) uses forms of energy other than high temperature to achieve crystallization and (2) creates short elemental diffusion distances to lower the energy necessary for atomic migration and crystallization. Using gaseous precursors and plasma co-reactants, the layer-by-layer growth mode of PEALD boasts conformal deposition of various carbides and nitrides at low temperatures (150-300 °C).**³** However, PEALD has yet to be demonstrated for synthesis of MAX-phase thin films.

By characterizing the stoichiometry and crystallinity of PEALD-grown films, our work explores the viability of PEALD for synthesis of MAX-phase Ti_2AlN. In this work, tetrakis(dimethylamido)titanium (TDMAT) and trimethylaluminum (TMA) precursors with N_2/H_2 plasmas are used for deposition of composite TiAlN films on SiO_2/Si and Al_2O_3 substrates, which are then annealed under various conditions. Our work shows that the Ti:Al ratio can be easily controlled by the TDMAT:TMA cycle ratio, while higher growth temperatures and H_2 plasma induce N-deficient TiN and Al layers for a stoichiometry closer to the composition of Ti_2AlN. Furthermore, annealing of PEALD-grown TiAlN is observed to induce desorption of Al and N, a mechanism seen in conventionally sputtered Ti/AlN composites that leads to formation of MAX-phase Ti_2AlN. The effects of contamination and as-deposited crystallinity on the final composition and structure of annealed PEALD-grown TiAlN are investigated.

[1]Barsoum, M. W. et al. (2000). *Prog. Solid. State Chem.*, *28*(1-4), 201-281.

[2]Eklund, P. et al. (2010). *Thin Solid Films*, *518*(8), 1851-1878.

[3]Profijt, H. B. et al. (2011). *J. Vac. Sci. Technol. A: Vac. Surf. Films*, *29*(5), 050801.

Acknowledgments: This work was supported by Battelle Savannah River Alliance, LLC under Contract No. 89303321CEM000080 with the U.S. Department of Energy and performed in part at the Georgia Tech Institute for Electronics and Nanotechnology, a member of the National Nanotechnology Coordinated Infrastructure, which is supported by the National Science Foundation (Grant ECCS-1542174).

11:00am **PS1+AP+TF-WeM-10 AVS Graduate Research Awardee Talk: Temporal Evolution of Densities and Temperatures in Sub-Microsecond Pulsed Microwave Discharges***, **Dhruval Patel**[1,2], T. Choi, H. Swearingen,* University of Illinois at Urbana Champaign*; D. Jacobson,* Lyten*; J. Bruehl,* University of Illinois at Urbana Champaign*; B. Gittleman, M. Stowell,* Lyten*; E. Barlaz, S. Dubowsky, D. Ruzic,* University of Illinois at Urbana Champaign

Material synthesis in plasma reactors have been long investigated as an alternative to more traditional thermochemical reactors. The promise of efficient reaction channels has extended the use of plasmas in synthesis of more exotic materials such as graphene. Ever since its discovery, tremendous effort has been put towards realizing a scalable plasma-based graphene synthesis process. However, further optimization of these reactors is still required before a commercially viable process can be achieved.

Non-thermal pulsed plasma discharges can provide a gateway to a more efficient conversion of methane, primarily due to enhancement of vibrational excitations. In such discharges, the electron, vibrational and rotational temperatures can vary over the duration of the pulse and must be accounted for to accurately describe the reaction kinetics. This work aims to obtain these temperatures along with densities of hydrogen in the methane discharge over the course of the pulses to both characterize the plasma and estimate methane cracking efficiency. We also consider the hydrogen radical density as this can be used as a proxy to understand the reactions mechanisms. To do so, time gated emission spectrums for the Ar-CH_4 plasmas are obtained and analyzed. The electron temperature is inferred from various $Ar2p_{10-1}$ – $Ar1s_{5,2}$ transitions spanning 690 nm - 815 nm. The vibrational and the rotational lines are determined by spectral fitting of C_2 swan bands or CH A^2D-^2C bands. Hydrogen densities are obtained using actinometry by using trace amounts of Kr (<0.5%). A simple model is used to deduce the approximate densities of hydrogen radicals by comparing the emission of H_b to Kr $3p_{9,8,6}$ (431.96 nm, 431.86 nm, and 427.4 nm) and H_a to Kr $2p_{3,2}$ (557.03nm and 587.09 nm). Combined, these measurements will provide valuable insight into the characteristics and breakdown efficiency of methane containing pulsed plasmas.

11:20am **PS1+AP+TF-WeM-11 In situ Atomic Layer Doping Coupled Low-temperature Epitaxial Growth of β-Ga_2O_3 Films via Plasma-enhanced ALD***, **Saidjafarzoda Ilhom**, A. Mohammad, J. Grasso,* University of Connecticut*; A. Okyay,* Stanford University*; B. Willis, N. Biyikli,* University of Connecticut

Wide bandgap (WBG) semiconductors, such as GaN and SiC make up the key components of high-power high-frequency electronic devices, such as, smart power grids, 5th generation (5G) technology, and electric transportation systems. However, production complexity and high cost of these materials make such technologies less available. Gallium oxide (Ga_2O_3) is an emerging ultra-WBG semiconductor attracting great attention due to its superior electrical properties (larger bandgap ~4.9 eV, high dielectric constant 6-8 MV/cm). Additionally, to compete against the mature WBG materials which are grown typically at 700 – 1000 °C, a substantially lower temperature deposition technique for crystalline Ga_2O_3 is of particular importance for its integration with temperature-sensitive substrates or device structures.

In this study, we report on the low-temperature deposition of crystalline Ga_2O_3 films on Si, sapphire, and glass substrates via hollow-cathode plasma-assisted ALD. Films were grown using triethylgallium (TEG) and Ar/O_2 plasma as metal precursor and oxygen co-reactant, respectively. Growth experiments have been performed at 240 °C substrate temperature and 50 W rf-power. Additionally, each unit AB-type ALD-cycle was followed by an *in situ* Ar-plasma annealing treatment, which consisted of Ar-plasma exposure for 20 seconds at 250 W rf-power. Furthermore, we have employed *in situ* atomic layer doping to n-type dope β-Ga_2O_3 films where tris-dimethylaminosilane (TDMAS) and tetrakis-dimethylaminotin(IV) (TDMASn) were utilized as the dopant precursors. The doping process was carried out via both supercycle (ABC-type ALD-cycle) and co-dosing methods. Both *in situ* and *ex situ* ellipsometry were employed to measure the thickness and optical properties of the films. The samples exhibited enhanced growth-per-cycle (GPC) values around 1.3 Å. X-ray diffraction (XRD) of the sample on sapphire revealed epitaxial Ga_2O_3 film signature with monoclinic β-phase. High-resolution transmission electron microscopy (HR-TEM) revealed the epitaxial relationship of the Ga_2O_3 layers grown on sapphire substrates. Further results from our ongoing structural and electrical characterizations will provide additional insight to overcome the challenges in achieving device quality undoped and doped β-Ga_2O_3 layers at low growth temperatures. Comparison of Si and Sn-doping strategies will be discussed, and if needed, ex-situ thermal annealing studies will be carried out for doping activation.

11:40am **PS1+AP+TF-WeM-12 Plasma-Polymer Coating of Li-Metal Anodes for the Improvement of Li-Ion Batteries***, **Yannik Moryson**, H. Hartmann, S. Otto,* Justus Liebig University Giessen, Germany*; X. Fang,* Technical University of Darmstadt, Germany*; M. Rohnke, J. Janek,* Justus Liebig University Giessen, Germany

The demand for batteries with higher energy densities for electro mobility and energy storage still raises the question for a working lithium metal anode in battery systems. The native passivation layer on top of Li-foils is not suited to enable stable cycling of corresponding electrochemical cells due to inhomogeneities and impurities in the layer composition. These inhomogeneities and impurities will result in locally varying current densities, which lead to dendrite growth and ultimately cell failure. Artificial protection layers are one promising option to overcome these drawbacks and enable the use of lithium anodes. Here, plasma polymer coatings are a quite promising approach.

In this study, we used a self-constructed inductively coupled radio frequency (rf) plasma reactor to clean Li-foils in a first step and after that performed plasma polymerization of 1.4 bis(trifluoromethyl)benzene to deposit a passivation layer on top of lithium metal anodes and characterized the layer with time-of-flight secondary ion mass spectrometry, x-ray photoelectron spectroscopy and scanning electron microscopy. The mechanical properties of the layer were examined by nanoindentation. The results were compared with a commercial Parylene HT polymer to verify the plasma polymerization process. Additionally, we performed $^{18}O_2$ isotopic exchange experiments to determine the diffusion coefficients of oxygen in untreated Li-foils at room temperature $D = 6.3 \pm 0.5 \cdot 10^{-20}$ cm²/s and for oxygen in the plasma polymer at room temperature $D = 3.0 \pm 0.2 \cdot 10^{-23}$ cm²/s, which showed the protective nature of the coating. Symmetric cell tests with the coated Li electrodes showed a stable cycling behavior for over 300 h with overpotentials below 0.1 V. The electrochemical performance was clearly improved in contrast to cells with uncoated Li.

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[1] **PSTD Coburn & Winters Student Award Finalist**

[2] **AVS Graduate Research Awardee**

12:00pm **PS1+AP+TF-WeM-13 Fabrication and Evaluation of Composite Thin Film Membranes for Tritium Management in Future Fusion Plants**, ***Adam Job***, *C. Li,* Colorado School of Mines; *T. Fuerst, C. Taylor,* Idaho National Laboratory; *J. Way, C. Wolden,* Colorado School of Mines

The hydrogen isotopes tritium and deuterium are leading fuels for use in future fusion reactors. While deuterium is relatively abundant and can distilled from seawater, tritium is a radioactive compound with a short half-life that must be continuously generated and recovered from lithium-based breeder blankets. Vanadium (V)-based membranes are a promising candidate for tritium recovery due its high hydrogen permeability, thermal stability, and neutron tolerance. However, they require application of a catalytic layer to efficiently dissociate/recombine hydrogen and maintain a clean surface. Platinum group metals (Pt, Pd) are effective catalysts but rapidly alloy with V and lose activity. We are developing nanoscale hydrogen-permeable intermetallic diffusion barriers deposited by techniques such as reactive sputtering and atomic layer deposition. In this presentation we describe the plasma cleaning and preparation of these foils as well as the deposition of ceramic nitrides and oxides barrier layers and catalysts layers. We developed a composite structure to efficiently evaluate the hydrogen permeability of these thin films, whose properties can be orders of magnitude different than their bulk counterparts. The performance and stability of these V-based nanocomposite hydrogen membranes was evaluated as a function of temperature and hydrogen pressure. The differences between successful and unsuccessful membranes is assessed and understood through the use of materials characterization including X-ray diffraction and compositional depth profiling using TOF-SIMS and Auger spectroscopy.

Plasma Science and Technology Division
Room 315 - Session PS2+TF-WeM

Plasma Processes of Non-Silicon Related Semiconductors for Energy-Efficient Devices in Power, Photovoltaics and Optoelectronics Applications

Moderators: Kenji Ishikawa, Nagoya University, Japan, **Steven Vitale**, MIT Lincoln Laboratory

8:00am **PS2+TF-WeM-1 Low-Damage Etching of Nitride Semiconductors Utilizing Photo-Electrochemical Reactions**, ***Taketomo Sato,*** Hokkaido University, Japan **INVITED**

Gallium nitride (GaN), which is a III-nitride semiconductor, has wide direct bandgap (3.4 eV), high breakdown electric field (3.3x10^6 V/cm) and high saturation electron velocity (2.7 x10^7 cm/sec). On the basis of excellent optical and electrical properties, significant progress has been achieved in the GaN and III-nitride based devices, such as ultraviolet laser diodes, white light-emitting diodes, and high-frequency power transistors.

For the fabrication of GaN-based devices, the etching process is one of the key-issues because GaN is a robust material with strong chemical bonds between nitrogen and Ga showing high chemical stability. Among the various etching technique, the photoelectrochemical (PEC) etching method has a great advantage in low damage and high controllability on nitride semiconductors. The PEC etching process consists of anodic oxidation of the surface and subsequent dissolution of the oxide with a chemical treatment. Since the photo-carriers generated near the sample surface is utilized to enhance the oxidation, the etching reactions easily occur even in highly-stable nitride semiconductors. In addition to this, the electrochemical reactions proceed at room temperature and follows Faraday's law. These features allow etching of nitride semiconductors with low damage and high controllability.

In this presentation, I introduce our recent work on the PEC etching of nitride semiconductors for high-power and high-frequency device application. As an example, the PEC etching process has been optimized for recess etching of AlGaN/GaN high electron mobility transistors (HEMTs), a key device in next-generation communication systems. The etching features were drastically changed with both the light wavelength and its irradiation power. Under the optimal condition, we obtained a very slow etching-rate of 0.12 nm/min, leading to a smooth and flat surface with rms-roughness of 0.4 nm. The threshold voltage (V_{th}) of recessed-gate AlGaN/GaN HEMT was precisely controlled by the residual AlGaN thickness after the PEC etching. These features are promising to realize the high-performance HEMTs with a normally-off operation.

8:40am **PS2+TF-WeM-3 Gan Profile Understanding During the Plasma Etching of an HEMT Recessed-Gate with a Photoresist Mask**, ***Simon Ruel,*** CEA-LETI, France; *P. Thoueille,* Lam Research Corporation, France; *P. Pimenta-Barros, N. Posseme,* CEA-LETI, France

GaN-based high electron-mobility transistors (HEMTs) constitute the next generation of high power devices after their silicon-based counterparts, because of their higher super-conducting properties offered by a two-dimensional electron gas (2DEG) channel created at the AlGaN/GaN heterojunction. For safety and consumption considerations, a Normally-Off operating mode is desirable, and possible by patterning the transistor gate with a full recess beneath the 2DEG in order to cut physically the conduction. To maximize the final device efficiency, the gate profile as well as the Plasma Induced Damage (PID) need to be well controlled. Therefore, it seems very important to understand the plasma interactions with the GaN and the associated mechanisms responsible for the GaN profile in order to better control it.

In this paper, we propose a morphological study of the gate plasma etching. The study is firstly composed of different tests and characterizations in order to understand and identify the mechanism responsible for the GaN profile. Then, the knowledge was applied to optimize the Process of Reference (POR) towards a more vertical and uniform profile.

After having opening Barc and dielectric layers, the AlGaN/GaN partial recess is done with a Cl_2/BCl_3-based RIE plasma with a photoresist mask. An etching film of the latter step was performed to identify the gate profile formation and eventual defects. We obtained a tapered profile (~50°) due to a polymer deposition on sidewall, growing with the etching time.

The characterization of these products was performed thanks to TEM EDX. The polymer may be mainly composed of C and Cl, with some traces of Ga. The presence of metallic traces explained the non-removal of the layer by an O_2 plasma.

A parametric study allows us to identify the key parameters responsible for the passivation regime and the slope control: the ElectroStatic Chuck Temperature (ESC T°), the amount of BCl_3 in the plasma, and the DC Bias voltage. Coupled with the previous analysis, we can propose a mechanism responsible for the sidewall passivation. Three main contributors are identified: a [C-Cl] compounds redeposition coming from the resist mask erosion, non-volatile Ga-based compounds [Ga-Cl] coming from the etched GaN trench, and a B_xCl_y contribution coming from the BCl_3 dissociation in the plasma.

Finally, we compared the best process obtained to the POR : it shows a more vertical and uniform GaN profile (80°) against a tapered profile with a double-slope (52°/65°) for the reference.

9:00am **PS2+TF-WeM-4 Quantitative Characterization of Plasma-Induced Defect Creation in InP Substrates Using Conductance Analysis**, ***Takahiro Goya,*** Kyoto University, Japan; *Y. Kodama, Y. Zaizen, M. Fukasawa,* Sony Semiconductor Solutions Corporation, Japan; *K. Urabe, K. Eriguchi,* Kyoto University, Japan

To meet increasing demands for higher operating frequency, new material-based systems that exceed the electron mobility limit of Si have attracted attention. InP is one of the promising semiconductors implemented in the next generation devices [1]. In designing the performance, the property degradation during plasma processing—plasma-induced damage (PID) [2]—is a critical issue. However, in contrast to Si devices, there have been no quantitative evaluation technique assessing the nature of PID in InP systems. In this study, we propose a defect characterization technique for InP systems using conductance analysis. N-type InP substrates were exposed to capacitively coupled plasma with Ar gas. Exposure time and peak–to–peak voltage (V_{pp}) were varied from 3 to 30 s and 270 to 450 V, respectively. We first confirmed that the present PID forms damaged layers on Si substrates whose thicknesses were approximately 5 nm by spectroscopic ellipsometry. 5.8 nm SiO_2 films were formed by ALD for electrical analyses. SiO_2/Si structures were prepared in comparison. It was revealed that tunneling current and capacitance-voltage tests (commonly employed in Si devices) were not sufficient to evaluate PID in InP systems. We applied a conductance technique [3] with an optimized equivalent circuit model. An AC modulation bias with a frequency (f_{mod}) from 100 Hz to 1 MHz was superimposed on a DC bias (V_{bias}). The peaks in conductance spectra for the SiO_2/InP devices were found to be "pinned" around 1 kHz after plasma exposure regardless of V_{bias} in depletion, whereas the peak shift in response to V_{bias} was observed for the SiO_2/Si devices. Moreover, the peak intensity for the SiO_2/InP devices increased with V_{pp}, while exposure time did not significantly impact strongly, presumably due to the dose dependence of the profile. These findings indicate that the nature of PID in InP substrates is unique, *i.e.*, the electrical response of created defects is different from that in Si devices. In addition, the PID can be quantified with the conductance method in terms of the peak intensity at a specific f_{mod}. The proposed conductance analysis is extremely useful for the PID assessment in future InP-based devices.

[1] W. R. Deal *et al.*, IEEE IEDM, 2016, p. 707.

[2] K. Eriguchi, J. Phys. D: Appl. Phys. **50**, 333001 (2017).

[3] T. Kuyama *et al.*, Jpn. J. Appl. Phys. **59**, SJJC02 (2020).

9:20am **PS2+TF-WeM-5 Impact of Bias Power and Oxygen Addition on Selective Dry Etching of TiAlC over TiN Using N_2/H_2-based Plasmas**, ***Kenji Ishikawa***, *T. Nguyen,* Nagoya University, Japan; *K. Shinoda, H. Hamamura,* Hitachi, Japan; *K. Maeda, K. Yokogawa, M. Izawa,* Hitachi High Technologies, Japan; *M. Hori,* Nagoya University, Japan

In the isotropic etching of multiple metal gate materials made of titanium compounds, selectivity of TiAlC against the other materials, involving metal compounds, insulators, and semiconductors, such as TiN, TaN, HfO_2, and C hard mask is required. Wet etching of Ti compounds using H_2O_2 mixtures has been conventional applied. However, this causes damage to the other exposed materials due to low etch rates and insufficient selectivity, as a result of a prolonged treatment time. To increase selectivity of etch rates for TiAlC films, the dry etching for ternary material TiAlC has been developed by processing with high density of radicals generated in a NH_4OH vapor plasma at medium-pressure plasma in our previous study [1]. This is feasible to show a potential of isotropic etching using chemistries containing NH and H.

In this study, selective dry etching of the ternary material TiAlC over TiN has been first developed using N_2/H_2-based plasmas generated from a capacitively coupled plasma etcher at low pressure. Using an *in situ* ellipsometry and an optical emission spectrometer (OES), highly selective etching of TiAlC over TiN has been investigated. In particular, addition of a small amount of O_2 (10%) into the N_2/H_2 plasmas enhanced the selectivity. A process window for selective removal of TiAlC over TiN is presented here at various bias powers, in which chemical etching was dominant at lower bias power with higher selectivity (>5). By using various mixtures of N_2, H_2, and O_2 gases for generating plasmas, surface reactions under energetic ion bombardments produces selective surface modification of the TiAlC and TiN films. Controlling O_2 addition and ion energy is essential for enabling applications of both selective anisotropic or isotropic etching of metal carbides, metal nitrides, or metal oxides.

11:00am **PS2+TF-WeM-10 Bulk Titanium Micromachining and Simultaneous Sidewalls Passivation for Bio-MEMS Applications**, ***Rim Ettouri***, *T. Tillocher, P. Lefaucheux,* GREMI CNRS/Université d'Orléans, France; *B. Boutaud, J. Phung, H. Philippe,* MISTIC, France; *R. Dussart,* GREMI CNRS/Université d'Orléans, France

The biomedical field has seen significant expansion because of the rise of microsystems. Even though silicon has historically been the material of choice, improvements in Titanium (Ti) micromachining have enabled the creation of bulk Ti-based devices. Whilst wet etching methods for Ti are available, they are isotropic and so restrict the geometry of features that may be created, especially at the microscopic scale. Conversely, Reactive Ion Etching (RIE) of titanium has allowed the formation of anisotropic profiles and the fabrication of biodevices such as vascular stents and micro-needles for drug delivery. In the literature, three distinct plasma chemistries for titanium dry etching have been reported with promising results: fluorinated, chlorinated, as well as combined chloro-fluorinated plasmas [1].

A method for simultaneous etching and sidewall passivation of bulk titanium is presented, which bypasses the conventional cyclic methods requiring separate passivation steps, such as the MARIO process [2]. Fundamentally enabled by the use of a continuous plasma of $SF_6/O_2/Ar$, the key novelty of this technique lies in the formation of a passivating oxide layer during micromachining . Iridescent oxide colors at the bottom of the etched Ti trenches were obtained, which result from the interference of light reflected from thin transparent oxides. Herein, we explain the oxidation mechanism that occurs during micromachining. Understanding the passivation schemes of Ti RIE is important for increasing feature aspect ratios and further miniaturization of the devices.

By adjusting the plasma parameters, the process can be controlled to achieve the best results in terms of etch rate and anisotropy while maintaining an acceptable undercut. The sidewall passivation material which is formed is found to be a titanium dioxide which contains only minor amounts of fluorine, giving the X-Ray Diffraction (XRD) patterns characteristic of rutile and anatase phases and as shown by the Energy Dispersive X-Ray Spectroscopy microanalyses (EDS). Fundamentally, the corresponding etching profiles strongly correlate the competitive effects based on the simultaneous etching and oxidation of the surface by atomic F and O, respectively.

While an almost infinite number of techniques have been used to form rutile titanium dioxide on any surface, this is yet the first time it has been reported to be achieved by RIE. This can lead to a significant increase in the potential of titanium bio-MEMS and even widen the field of application.

[1] F. Fracassi, R. d'Agostino, Pure and Applied Chemistry 64 (1992) 703-707.

[2] M.F. Aimi et al., Nature Materials 3 (2004) 103-105.

11:20am **PS2+TF-WeM-11 Selective Dry Etching of TiAlC over TiN using N_2/H_2 Plasma Chemistry**, ***Thi-Thuy-Nga Nguyen***, Nagoya University, Japan; *K. Shinoda, H. Hamamura,* Hitachi, Japan; *K. Maeda, K. Yokogawa, M. Izawa,* Hitachi High-Tech, Japan , Japan; *K. Ishikawa, M. Hori,* Nagoya University, Japan

Selective etching of metal gate materials such as TiAlC over TiN is required in advanced fabrication of fin-type or nanosheet field effect transistor (FET) of logic semiconductor devices. The conventionally wet etching of TiAlC and TiN films using H_2O_2 mixtures causes poor etching performance and device damage. In contrast, dry etching shows advantages in controlling etchant species and their energies for both isotropic and anisotropic processes. In order to obtain higher selectivity between Ti compounds, a non-halogen chemistry for highly selective and controllable dry etching of TiAlC over TiN was reported in our previous study, which developed a feasible dry etching method for ternary material TiAlC using a high-density plasma at medium pressure [1]. For the semiconductor application, in this study, low-pressure dry etching of the ternary material TiAlC has been first developed by using N_2/H_2 plasma.

A capacitively coupled plasma etcher was used to generate N_2/H_2 plasmas, and the upper and lower electrodes were operated with 100 MHz and 2 MHz sources, respectively. Optical emission of an NH molecular line at 336.3 nm from N_2/H_2 plasmas was detected by an optical emission spectrometer (OES). The N_2/H_2 plasma can produce etchant species including NH, N, and H to form volatile products. The etch rate of TiAlC was around 2 nm/min for the N_2/H_2 plasma, whereas no etching occurred with only N_2 plasma or H_2 plasma. Selective etching of TiAlC to TiN has been successfully demonstrated.

The influence of substrate temperature on etch rate and selective etching of TiAlC over TiN was investigated in a range of -20°C to 50°C. The surface modification of the TiAlC and TiN films after plasma exposure was analyzed by X-ray photoelectron spectroscopy (XPS). The XPS analysis revealed that the modified layer that included N-H and C-N bonds formed only on TiAlC and not on TiN. This non-halogen plasmas etchingmethod can be applied for highly selective etching of metal carbides, nitrides, or oxides, based on proposed mechanisms for selective etching of TiAlC over TiN.

[1] T.T.N. Nguyen et al., AVS67, PS-Contributed On Demand-10 (2021).

11:40am **PS2+TF-WeM-12 Surface Modification of CoSi through Interconnect Fabrication Processes**, ***Nathan Marchack***, *A. Orefice, M. Hopstaken, G. Cohen, C. Lavoie, R. Bruce, C. Chen,* IBM Research

The introduction of copper BEOL interconnects played a critical role in downscaling CMOS technologies. However, at the dimensions required for future technology nodes, this mainstay faces its own set of scaling challenges, such as liner thickness limits and grain boundary scattering. [1] Topological semi-metals possess unique physical properties that make them promising candidates for the next generation of interconnect materials: namely, their resistance-area (RA) product decreases with decreasing thickness. One such material, CoSi is particularly attractive due to its compatibility with existing CMOS integration schemes. [2]

In order to facilitate patterning of semi-metals at competitive node dimensions, it is essential to investigate the influence of fabrication processes (e.g. plasma etching) on the bulk and surface properties. [3] We present surface analysis of subtractive halogen-based plasma etching of CoSi films, including effects on film stoichiometry characterized by XPS.

Downstream plasma and wet solution treatments for removal of the damaged surface layers are also presented. It was found that a cyclic approach, comprising alternating exposures of inductively coupled HBr and microwave downstream H_2 plasma, provides the best stoichiometric retention. Finally, the impact of different deposition methods to form CoSi is discussed, with particular focus on the grain size disparities observed.

[1] C.-L. Lo et al., J. App. Phys. 128, 080903, 2020.

[2] C.-T. Chen et al., IEEE Int. Electr. Dev. Meeting, San Francisco, CA, Dec 12-18th, 2020.

[3] N. Marchack et al., J. App. Phys. 130, 080901, 2021.

12:00pm **PS2+TF-WeM-13 PbS Quantum Dots Thin Film Dry Etching**, ***Nicolas Le Brun**,* LTM - MINATEC - CEA/LETI, France*; P. Gouraud,* STMicroelectronics, France*; G. Cunge,* LTM - MINATEC - CEA/LETI, France*; L. Parmigiani, S. Allegret-Maret,* STMicroelectronics, France

Nowadays there is an increasing demand to enhance the capabilities of industrial products to sense their environment more efficiently, i.e. under difficult conditions (smoke, darkness…). This challenges semiconductor manufacturers because applications concern many daily life products using image sensors (smartphones, cars, automated tools…etc).

One solution studied recently is to extend the capabilities of image sensors to detect light towards the near Infrared (NIR) and Short-wave Infrared (SWIR) regions . Silicon having weak absorption properties at these wavelengths, manufacturers are looking to develop new materials which could be efficient sensors for these specific regions of the light spectrum.

To this end, quantum dot thin films are promising materials for their tunable band gap, their absorption properties, and their large-scale production availableness.

This study is related to the elaboration of sensors using PbS quantum dot thin films, and will focus on its patterning through a dry etching step. We propose to compare different etch chemistry combinations to define the best etch condition to pattern our PbS quantum dot thin films. In order to ensure the best optical properties of our material, it is crucial to control the slope of the etched profile and to prevent the uncontrolled diffusion of etchant in the quantum dot thin film stack. We will therefore monitor these key parameters under various plasma chemistry combinations as well as other dry etching settings, such as temperature or pressure.

Smart Multifunctional Materials for Nanomedicine Focus Topic
Room 301 - Session SM-WeM
Smart Multifunctional Materials for Nanomedicine and Theranostics

Moderators: Diego La Mendola, University of Pisa, Italy, **François Reniers**, Université Libre de Bruxelles, Belgium, **Cristina Satriano**, University of Catania, Italy

8:40am **SM-WeM-3 Plasma-Enabled Switchable Surfaces: Going from Molecules to Bacteria***, U. Cvelbar, **Martina Modic**,* Jozef Stefan Institute, Slovenia **INVITED**

Switchable and smart surfaces have been a goal in the chemistry community for more than a decade. Although much work has been done in converting surface functionalities going from one function to another, like multiple times reported hydrophobic to hydrophilic or reversible, little has been understood beyond surface morphology, surface energies and surface chemistry initiated. The case of switchable surfaces became even more complex when dealing with macromolecules going down to macro objects like viruses or bacteria. Here plasmas offer a unique opportunity to modify surfaces, not only chemically but also on the atomic scale, interfering and modifying or exchanging chemical bonds in materials or their crystal structures. For this reason, this lecture will try to challenge these ideas, address them on a nanoscopic level and present an overview of results ranging from simple surface properties, macromolecule interactions and at the end, effects on viruses and bacteria interacting with these surfaces.

9:20am **SM-WeM-5 Cisplatin-Loaded Pd Nanoparticles as Bimodal Theranostic Nanomedicine in the Tumor Treatment***, A. Bellissima, G. Scivoletto, L. Cucci, V. Sanfilippo,* University of Catania, Italy*; A. De Bonis,* University of Basilicata, Italy*; R. Fiorenza, S. Scirè,* University of Catania, Italy*; V. Notarstefano, E. Giorgini,* Polytechnic University of Marche, Italy*; **Cristina Satriano**,* University of Catania, Italy

In this work, we developed a hybrid nano delivery system made of palladium nanoparticles (NPs) and cisplatin (CisPt), an alkylating drug commonly used to treat various types of malignancies. NPs were synthesized via a new green method based on the use of D-glucose and polyvinylpyrrolidone (PVP) as reducing/stabilizing and capping agents, respectively. Plasmonic properties and photocatalytic activity of the Pd NPs, carried out to prove their capability to act as bimodal theranostic nanomedicine, unveiled a plasmon peak at around 274 nm, well matching an optical size of 5 nm for spherical nanoparticles, and significant H_2 evolution. XPS, XRD, and TEM confirmed the chemical composition and morphology of the NPs. The hybrid NP-drug assembly (Pd@CisPt) was characterized by UV-visible spectroscopy to correlate the changes in the plasmonic peak to the interaction of CisPt with the NP surface as by ICP-OES, to quantitatively estimate the drug loading. AFM and DLS measurements confirmed the strong association of the drug to the nanoparticle surface. The SOD-like activity was tested in a cell-free environment to confirm the maintenance in the Pd@CisPt sample of the antioxidant capability of Pd nanoparticles. The Pd@CisPt theranostic nano platform was tested in prostate cancer cells (PC-3 line) in terms of cytotoxicity, to prove the antitumoral action of the developed nanomedicine. Raman microspectroscopy (RMS) with PCA indicated a condition of protein misfolding/unfolding, directly or indirectly due to cisplatin and/or palladium treatment, and DNA damage especially enhanced upon the treatment with PdNPs@CisPt. The MitoSOX assay confirmed an increase in ROS generation, thus proving that oxidative damage is a key factor for the induction of antitumoral action. LSM cell imaging evidenced dynamic processes at the level of subcellular compartments and modulation of intracellular copper ions accumulation. Finally, cell migration studies upon the treatment with Pd@CisPt evidenced an intermediate response between the inhibitory effect by CisPt and the enhanced rate of cell migration for the metal NPs alone, which pointed out the promising potential of the developed theranostic nanomedicine in tissue regeneration.

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9:40am **SM-WeM-6 Old Drugs for a Golden Future: Clinically Established Au-Based Complexes…from Repurposing to Potential Application in Nanomedicine***, **Tiziano Marzo**, L. Chiaverini, D. La Mendola,* University of Pisa, Department of Pharmacy, Italy

Inorganic compounds played a key role in the pioneering times of modern pharmacology starting from the late 19th century. Gold, Bismuth, Antimony, but also Mercury compounds were widely used to treat a variety of diseases, mostly infectious, such as tuberculosis and syphilis, and a variety of parasitic diseases.[1,2] Their use in recent time underwent a rapid decline mainly because of concerns on their systemic toxicity. However, some Gold, Platinum or Arsenic compound is still widely used for clinical applications. Among them, antiarthritic compounds such as Auranofin (AF) or Aurothiomalate (ATM) found important role as repurposed drugs for treating cancer or infections.[3] Interestingly, the medicinal properties of gold(I) compounds might be even improved using biocompatible nanostructures for their delivery.[4] In this frame, we proceeded with the preparation of a nanoformulation of Et_3PAuCl, this latter being an AF analogue endowed with promising anticancer properties. The well-known PLGA-PEG nanoparticles (NPs) were chosen for the encapsulation process and functionalized with a biocompatible fluorescent probe for their tracking in cell. After the characterization of the NPs, we performed a few biological tests on the Et_3PAuCl loaded nanoparticles in comparison to the free Et_3PAuCl drug in 2D and 3D (HCT-116) colorectal cancer models. The biological activity and the mechanistic aspects for the anticancer effects of the loaded NPs are comparatively and critically discussed.

1-E. J. Anthony, E. M. Bolitho, H. E. Bridgewater, O. W. L. Carter, J. M. Donnelly, C. Imberti, E. C. Lant, F. Lermyte, R. J. Needham, M. Palau, P. J. Sadler, H. Shi, F.-X. Wang, W.-Y. Zhang and Z. Zhang,Chem. Sci., 2020,11, 12888-12917.

2- D. Cirri, F. Bartoli, A. Pratesi, E. Baglini, E. Barresi, T. Marzo, Biomedicines, 2021, 9(5), 504.

3- T. Marzo, D. La Mendola, Inorganics, 2021, 9, 46.

4- A. Menconi, T. Marzo, L. Massai, A. Pratesi, M. Severi, G. Petroni, L. Antonuzzo, L. Messori, S. Pillozzi, D. Cirri, Biometals, 2021, 34, 867–879.

11:00am **SM-WeM-10 Plasmonic Tuning of Go-Based Nanosheets by Plasmonic Noble Metal Nanorods for Self-Cleaning Photothermal Surfaces to Fight Surface Contamination***, **Vanessa Sanfilippo**, T. Pascal, A. Foti,* University of Catania, Department of Chemical Sciences, Italy*; A. Fraix, S. Petralia, G. Forte,* University of Catania, Department of Drug and Health Sciences, Italy*; C. Fortuna,* University of Catania, Department of Chemical Sciences , Italy*; A. Giuffrida, C. Satriano,* University of Catania, Department of Chemical Sciences, Italy

In this study, we propose a novel hybrid 2D nanomaterial based on thiolated reduced graphene oxide (rGOSH) sheets and silver (Ag) or gold (Au) nanorods (NRs). The goal is to integrate the enhanced self-cleaning properties (super-hydrophobicity) and the plasmonic tuning of photothermal response of the hybrid nanoplatform (GO-NR), to the intrinsic antibacterial properties of each component (GO, Ag, Au), to inhibit surface contamination. Both experimental and theoretical studies were focused on the design, the synthesis, and the physicochemical/biochemical/cellular characterization of the hybrids. A multitechnique approach by UV-visible spectroscopy (UV-VIS), dynamic light scattering (DLS), Zeta potential (ZP), atomic force microscopy (AFM), and water contact angle (WCA) measurements was used to scrutinize the plasmonic features (including the optical size), the hydrodynamic size and the surface charge, the topography and the surface free energy, respectively. The photothermal properties of the hybrids were examined in solution following the increase of temperature under irradiation with CW laser using a FLIR C3 thermal imaging camera. Proof-of-work *in vitro* cellular experiments on human prostate cancer cells (PC-3 line) and murine fibroblasts (L929 line) were carried out to test the nanotoxicity of the hybrids as well as their capability to induce oxidative stress by the production of reactive oxygen species (ROS). Intracellular imaging using confocal laser scanning microscopy (LSM) was performed to evaluate the mechanism of interaction and internalization of hybrid systems on the studied cell lines.

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11:20am **SM-WeM-11 Green Synthesis of Metal Nanoparticles for Wound Healing Applications***, **Alice Foti**, V. Sanfilippo,* University of Catania, Italy*; V. Caruso, R. Inturri, P. Amico, S. Vaccaro,* Fidia Farmaceutici S.p.A., Italy*; C. Satriano,* University of Catania, Italy

Wound healing is a complex process involving multiple cell strains and the related products trying to regenerate and repair the damaged tissue. The multidisciplinary field of nanotechnology that includes, among others, interface and colloid science, molecular biology, and engineering, offers a huge range of applications, including nanomedicine. Metallic nanoparticles (NPs), 1-100 nanometers (nm) in size, have unique physicochemical, optical, and biological properties that gives them a great potential in treating several diseases. Indeed, it is essential to find controlled and reproducible synthetic methods to achieve biocompatibility and the desired therapeutic properties, giving a ground-breaking approach towards the promotion of wound healing. This work focuses on a green synthesis approach to synthesize gold (Au), silver (Ag), and palladium (Pd) NPs, aiming to promote the proliferation of cells in wound healing. Moreover, NPs surface, is capped with hyaluronic acid (HA), known to improve their biocompatibility and promote endothelial regeneration. Physicochemical and biological characterization of the synthesized NPs was assessed with a multi-technique approach. Optical properties were studied with UV-vis spectroscopy; the increase of the hydrodynamic diameter after the conjugation with HA was investigated with dynamic light scattering (DLS) experiments; and the measurement of viscosity was performed with a viscosimeter. Biological tests were assessed on fibroblast (L-929) cells. Particularly, cytotoxicity was inspected via MTT assay; wound healing potential was investigated by *in vitro* wound scratch assay; sub-cellular interactions were analyzed with confocal microscopy.

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11:40am **SM-WeM-12 Nanoparticles Loaded with Histidine Rich Peptides for Wound Healing***, **Diego La Mendola**,* Università di Pisa, Italy*; L. Chiaverini, T. Marzo,* University of Pisa, Italy

The histidine-proline-rich glycoprotein (HPRG) is a single polypeptide chain protein of 70–75 kDa, with a multidomain structure. In humans, the protein is synthesized in the liver and is present in plasma at relatively high concentrations of 100–150 µg/mL (1.5 µM) [1]. HPRG ability to simultaneously interact with a large number of protein ligands and has been implicated in the regulation of various physiological and pathological processes including the formation of immune complexes, apoptotic/necrotic and pathogen clearance, cell adhesion, antimicrobial activity, anti-/pro-angiogenic activity, coagulation and fibrinolysis. Interestingly, these processes are often associated with sites of tissue injury or tumour growth, where the concentration and distribution of copper and zinc ions is known to vary.

In this work, we tackled the assembling of hybrid platforms made of gold or silver nanoparticles (NPs) functionalized with the peptides belonging to HPRG protein, and rich in histidine residues, in order to achieve a modulation of the angiogenic process in the wound healing treatment in presence/absence of divalent metal ions.

These new systems exploit the synergic effects of different components in the regeneration of damaged tissues.

Nanoparticles were characterized by UV-visible spectroscopy, to scrutinise the peptide binding to Au, by monitoring the changes in the plasmonic peak (AuNP). Atomic force microscopy and dynamic light scattering analyses confirmed a strong association of the peptides to the plasmonic nanoparticles.

Cellular experiments on human foreskin fibroblasts demonstrated the low cytotoxicity of the hybrid assemblies and their high ability to promote wound closure and fibroblasts migration. The activity of Au-GO-ANG were also tested in the presence of copper and/or zinc ions. Besides, cell imaging by confocal microscopy revealed synergic dynamic processes modulated by the different sub-cellular structures (lysosomes, mitochondria, cell cytoskeleton). The obtained results evidence the promising applications of the synthesized nanoparticles for wound care treatment and tissue regeneration.

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[1] K.M. Priebatsch, M. Kvansakul, I.K.H. Poon, M.D. Hulett, Biomolecules, 2017, 7, 22.

Surface Science Division
Room 319 - Session SS1+HC-WeM

Alloy Surface Reactivity

Moderator: Zdenek Dohnalek, Pacific Northwest National Laboratory

8:00am **SS1+HC-WeM-1 Development of a Predictive Model for Nb_3Sn Thin Film Growth: Elucidating the Substrate-Mediated Diffusion Pathways Guiding Alloy Formation in Accelerator Infrastructure***, **Sarah Willson**,* University of Chicago*; R. Farber,* University of Kansas*; S. Sibener,* University of Chicago

Niobium is the current standard elemental material for superconducting radiofrequency (SRF) cavities, but the required operating temperatures (< 4 K) impose a significant monetary burden. To achieve improved accelerating gradients at increased operating temperatures, efforts are underway to vapor deposit Sn on preexisting Nb SRF cavities to form Nb_3Sn thin films. However, these Nb_3Sn coatings contain high surface defect densities and stoichiometric inhomogeneities; the accelerating performance of Nb_3Sn coated cavities is directly associated with the Nb_3Sn surface morphology. Current Nb_3Sn SRF cavities, therefore, are impractical for implementation in particle accelerator facilities. The implementation of Nb_3Sn SRF cavities necessitates a comprehensive and mechanistic understanding of how to form smooth and homogenous Nb_3Sn films.

To develop a predictive growth model for Nb_3Sn grown *via* Sn vapor deposition, we aim to understand the interplay between the underlying Nb oxide morphology, Sn coverage, and Nb substrate heating conditions on Sn wettability, intermediate surface phases, and Nb_3Sn grain growth dynamics. In this work, Nb-Sn intermetallic species are grown on a single crystal Nb(100) in an ultra-high vacuum chamber equipped with *in situ* surface characterization techniques including Auger electron spectroscopy (AES), x-ray photoelectron spectroscopy (XPS), and scanning tunneling microscopy/spectroscopy (STM/STS).

Sn adsorbate behavior on oxidized Nb was examined by depositing Sn with sub-monolayer precision at varying Nb sample temperatures (T_S). STM data of Sn deposited on a highly ordered NbO surface reconstruction reveal that the Nb T_S during deposition strongly dictates the competition between Sn incorporation and desorption during subsequent annealing. By tailoring Sn deposition parameters to suppress Sn desorption, AES and XPS data of annealed intermetallic adlayers provide supporting evidence of how Nb substrate oxidization and sample temperature impact Nb-Sn coordination. Ongoing experimental studies aim to demonstrate the impact of altering numerous vapor and substrate conditions on the growth mechanisms and alloying dynamics that ultimately enable optimal Nb_3Sn growth.

8:20am **SS1+HC-WeM-2 Surface Chemical Reactions in the Oxidation of NiCr and NiCrW Alloys*, Petra Reinke*, *C. Volders,* University of Virginia, USA*; V. Avincola Angelici ,* University of Virginia*; I. Waluyo, A. Hunt,* Brookhaven National Laboratory*; L. Arnadottir,* University of Oregon**

The oxidation of alloys including several reactive elements is controlled by complex reaction pathways where surface chemistry, reactant transport, alloy microstructure, oxide-alloy epitaxy and other factors compete. Our work focusses on the oxidation of Ni-based superalloys frequently used in technologies subjected to a wide range of environmental stressors from chemically aggressive solutions in sea water, batteries and fuel cells to radiation in nuclear waste containers. We address the socalled “third element effect” TEE where a relatively small addition of a specific element has an outsized impact on corrosion and oxidation processes. We specifically address the initial steps in the formation of the protective oxide layer starting with a pristine alloy surface. Significant gaps exist in the mechanistic understanding of the initial reaction steps of their oxidation. Near ambient pressure X-ray photoelectron spectroscopy, XPS and STM were used to study the oxidation with O_2*in operando* for a sequence of alloy compositions from Ni-5wt%Cr, Ni-15wt%Cr, Ni-30wt%Cr to Ni-15wt%Cr-6wt%W. The experiments were performed at 500 °C, $p(O_2)=10^{-6}$ mbar and reflect the initial 25 ms of oxidation at ambient conditions. The formation of Ni and Cr oxides competes under these conditions due to kinetic limitations imposed on the reaction of Cr, which is thermodynamically preferred.

The comparison of oxide evolution for four different alloys with variable Cr and W content quantifies the outsized impact of W as a minor alloying element. For the binary alloys an initial rapid increase in chromia driven by Cr-surface enrichment is followed by NiO nucleation and growth, ultimately seeding a dual-layer structure. The addition of small amounts of W in Ni-15wt%Cr-6wt%W shifts the reaction pathways towards Cr oxidation revealing a high quality chromia layer which is desirable for its protective function. Density functional theory calculations inform that W atoms adjacent to Cr sites embedded in the Ni surface create even more favorable oxygen adsorption sites. In short, a larger Cr content in the surface enhances reaction with oxygen, but the addition of W “supercharges” the reactivity of Cr by funneling the oxygen atoms into Cr sites. The surface chemistry is identified as a decisive contribution to the TEE, and is accompanied by a enhanced grain boundary driven Cr transport in the alloy to sustain chromia growth.

8:40am **SS1+HC-WeM-3 High Throughput Methods for Comprehensive Study of Alloy Segregation and Structure Sensitivity*, Andrew Gellman*, *C. Fernandez-Caban, Z. Guo, R. Burnley,* Carnegie Mellon University, USA INVITED**

Comprehensive study of phenomena such as segregation in alloys or structure sensitivity in catalytic surface chemistry is hampered by the fact that the independent variables associated with these phenomena are continuous and multidimensional. In the case of alloy segregation, the relevant independent variable is alloy composition which is continuous and multidimensional in the case of ternary or higher order alloys. In the case of structure sensitivity, the possible orientations of single crystal surfaces span a continuous 2D space. Comprehensive study of these phenomena requires high throughput methods that allow rapid, concurrent measurements of surface composition and chemistry across parameter space.

Composition spread alloy films (CSAFs) have been used as sample libraries for accessing broad and continuous alloy composition spaces. CSAFs are thin alloy films deposited on appropriate substrates such that they have lateral composition gradients. A binary CSAF of components A and B can run from pure A at one end to pure B at the other. A ternary CSAF can be prepared with a triangular region that mimics a ternary composition diagram and literally contains all possible ternary alloy compositions. These alloy sample libraries are ideal for the study of surface segregation. We have used low energy He^+ ion scattering to map segregation at 100s of alloys spanning the composition spaces of CuPdAu, CuAgAu and NiPdAu ternaries. This work has explored both equilibrium segregation over a range of temperatures and the measurement of surface segregation kinetics.

Surface Structure Spread Single Crystals (S^4Cs) have been used as sample libraries for accessing broad and continuous ranges of single crystal surface orientations. S^4Cs are metal single crystal disks fabricated such that one side is a section of a sphere. These usually (but not necessarily) have a low Miller index plane exposed at their center and the rest of the surface exposing all possible surfaces orientations lying within some polar angle (14° in our case) of the low Miller index point. By first adsorbed reactive species on the curved surface and then spatially mapping their coverage versus time, $\vartheta_{hkl}(t)$, at a given temperature we are able to extract reaction rate constants as functions of surface orientations. In this manner, we have studied the enantiospecific decomposition kinetics of D- and L-tartaric acid on all chiral Cu(*hkl*)R&S surfaces vicinal to the three low Miller index planes.

9:20am **SS1+HC-WeM-5 Unveiling the Ability of Rh Single Atoms to Enhance the Dissociation of Molecular Oxygen and Spillover to Cu*, Volkan Cinar*[1], Tufts University*; D. Guo,* Washington State University, US*; Y. Wang, C. Easton, H. Chen,* Tufts University*; N. Ulumuddin,* Washington State University, US*; R. Hannagan,* Tufts University*; I. Waluyo,* Brookhaven National Laboratory*; J. McEwen,* Washington State University, US*; C. Sykes,* Tufts University**

Copper-based catalysts are used in a wide range of heterogeneous catalytic processes such as methanol synthesis, CO oxidation, epoxidation of alkenes, and the water-gas shift reaction. As many of these reactions can take place in oxidizing environments, CuO_x surfaces have been extensively studied to better understand structure-function relationships. Single-atom alloys (SAAs) are a new type of catalyst in which small amounts of reactive dopants (Pd, Pt, Ni, Rh, etc.) are present as isolated atoms in less reactive metals such as Cu. However, literature of the behavior of these materials under oxidizing conditions is limited.

Using surface science experiments we discover that 0.005 monolayers Rh in the surface of Cu(111) enhances the rate of O_2 dissociation by ~20 times. TPD experiments are conducted using the partial oxidation of methanol to formaldehyde to titrate away the adsorbed oxygen and hence quantify the increased dissociative sticking probability of O_2 on the RhCu SAA vs. Cu(111). CO “poisoning” and annealing experiments were conducted to further investigate the role of the Rh atoms in dissociating molecular oxygen. These TPD experiments reveal that adsorption of ~1% of a monolayer of CO, which block the Rh sites and reduce the O_2 dissociation back to pure Cu(111) providing evidence that Rh is the site for O_2 activation. Furthermore, annealing the surface to 250°C, which induces the subsurface diffusion of Rh, gives the same result. Further quantification of oxygen uptake on the RhCu SAA reveals a spillover effect whereby molecular oxygen dissociates on the Rh atom sites and diffuses to sites on Cu(111). STM experiments are performed to elucidate the atomic-scale detail of this effect. The STM images reveal that on Cu(111) and the RhCu SAA, oxidation occurs at the Cu step edges, consistent with literature reports. However, for the case of the RhCu SAA, we observe features on the terraces, consistent with atomic oxygen spill over from Rh atoms. Our DFT calculations quantify the energetics of the process showing that the molecular oxygen binds to the Rh sites stronger than Cu(111) and that the activation barrier is lower as compared to bare Cu(111). Furthermore, our DFT results support the spillover of oxygen atoms from Rh site to the Cu host. Together, these results begin to shed light on the role of single metal atom dopants in promoting Cu oxidation.

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[1] **SSD Morton S. Traum Award Finalist**

Surface Science Division
Room 319 - Session SS2+AS+HC-WeM

Nanoparticle Surfaces

Moderator: Zdenek Dohnalek, Pacific Northwest National Laboratory

9:40am **SS2+AS+HC-WeM-6 Understanding the Growth of Sn and Pt-Sn Clusters on Titania and Carbon Surfaces***, S. Beniwal,* University of South Carolina*; W. Chai,* University of Texas at Austin*; M. Qiao, P. Kasala,* University of South Carolina*; K. Shin, G. Henkelman,* University of Texas at Austin*; **Donna Chen,*** University of South Carolina

Supported Pt-Sn bimetallic clusters have applications in number of catalytic processes, including dehydrogenation of alkanes and selective hydrogenation of unsaturated aldehydes. In these reactions, the presence of Sn is known to promote the desired selectivity of the Pt-based catalyst. However, the chemical activity the supported Pt-Sn catalysts is dependent on the Sn oxidation state and the nature of Sn interaction with the support, as well as dispersion. Sn and Pt-Sn clusters have been vapor-deposited on $TiO_2(110)$ and highly oriented pyrolytic graphite (HOPG) and studied by scanning tunneling microscopy, X-ray photoelectron spectroscopy, and low energy ion scattering. Deposition of Sn on titania results in the formation of small, uniformly sized clusters with SnO_x at the cluster-support interface and reduction of the titania support. Subsequent deposition of Pt produces exclusively bimetallic clusters, and Sn diffuses away from cluster-support, resulting in a decrease in SnO_x and Sn-rich cluster surfaces. Density functional theory (DFT) calculations demonstrate that M-TiO_2 bonding is favored over M-M bonding for M=Sn, unlike for transition metals such as M=Pt, Au, Ni, and Co. Furthermore, the substantial charge transfer from Sn to TiO_2 leads to dipole-dipole repulsion of Sn atoms that prevents agglomeration into the larger clusters that are observed for the mid-late transition metals. DFT studies also confirm that addition of Pt to a Sn cluster results in strong Pt-Sn bond formation and diminished Sn-O interactions. In the case of Sn deposition on HOPG, the clusters are surprisingly small given that Sn does not interact strongly with the support, whereas other metals such as Pt, Re and Pd readily diffuse to form large clusters that aggregate at step edges. DFT investigations show that Sn is unique in that the per atom binding energy of Sn in small clusters (<15 atoms) is as low as 0.14 eV/atom compared to Sn atoms in the bulk; for Pd, Pt, and Re, the binding energy is 0.9-1.9 eV/atom. Therefore, it is thermodynamically favorable for Sn to form small clusters and for other metals to form large clusters.

11:00am **SS2+AS+HC-WeM-10 Single Nanoparticle Surface Chemistry: Structure-Reactivity Relationships, Evolution During Reactions, and an Approach to Ultra-High Temperature Surface Chemistry***, C. Lau, A. Friese, D. Rodriguez, **Scott Anderson,*** University of Utah

Nanoparticles (NPs) are inherently heterogeneous, with variations in size, shape, and distributions of reactive sites. This talk will explore the kinetics for oxidative etching of *individual* carbon and silicon NPs, tracking changes in reactivity as the NP structure evolves under reaction conditions.

Examples of O_2 oxidation of typical carbon black and graphene oxide NPs is shown in the figure, which shows the NP mass vs. time at 1200 K under inert (unshaded background) and oxidizing conditions (cyan background). The lower frames show how EE_{O2}(the etching efficiency in terms of Da of mass lost *per* O_2 collision) varies with the NP mass. Oxidative etching of carbon NPs varies significantly between NPs from different feedstocks, but there are also variations between NPs from the same feedstock, reflecting variations in the distributions of surface sites. Furthermore, the reactivity of individual NPs evolves non-monotonically in time as the NPs etch, with rate fluctuations of up to 5 orders of magnitude. Eventually, all carbon NPs become nearly inert to O_2, signaling that the surface layer(s) have transformed to multiwall fullerene-like structures.

For silicon NPs, we are able to study oxidation over a temperature range from 1200 to 2500 K, spanning the bulk T_{melt} of both silicon and silica. Etching involves several interacting processes that depend differently on temperature and time, thus etching of silicon-based NPs can have quite complex time dependence. For example, at temperatures (e.g. 1200 K) well below the silicon melting point (T_{melt} = 1683 K), the etching mass loss rate is initially low, accelerating as etching progresses, then eventually dropping several orders of magnitude to ~zero as the NP surface grows a passivating silica layer. At temperatures closer to the melting point (e.g. 1500 K), the oxidative mass loss rate starts high and remains high as the NP loses 15 – 30% of its initial mass, then abruptly drops to near zero as the surface passivates. For temperatures above T_{melt}, the etch rate begins to decrease immediately upon O_2 exposure, but it never drops to zero, i.e., the NP surface never passivates.

One of the features of this method is that the upper temperature possible is limited only by the sublimation rate of the particle's material. Thus for Si, it is straightforward to examine temperatures well above T_{melt}. For ultra-high temperature ceramic materials, it is possible to study surface chemistry at temperatures to well above 3000 K. Oxidation of HfC ($T_{melt} \approx$ 4200 K), will be used to illustrate this capability.

11:20am **SS2+AS+HC-WeM-11 Oxidation of Size-Selected Ag Clusters on Graphene: Bulk Motifs and Electronic Anomalies at sub-Nanoscale***, F. Loi,* University of Trieste, Italy*; M. Pozzo,* University College London, UK*; **Luca Bignardi**, L. Sbuelz,* University of Trieste, Italy*; P. Lacovig, E. Tosi, S. Lizzit,* Elettra Sincrotrone Trieste, Italy*; A. Kartouzian, U. Heiz,* Technical University Munich, Germany*; R. Larciprete,* Institute for complex systems - CNR, Italy*; D. Alfè,* University College London, UK*; A. Baraldi,* University of Trieste, Italy

The evolution of the aggregation of condensed matter from single atoms to three-dimensional structures represents an crucial topic in nanoscience since it contains essential information to achieve tailor-made growth of nanostructured materials. Such issue is particularly important in the case of the formation of nano-oxides, which have strong potentialities in heterogeneous catalysis reactions. In this respect, we investigated the oxidation of an Ag nanocluster composed of 11 atoms supported on epitaxial graphene on Ru(0001), combining synchrotron-based core-level photoelectron spectroscopy and *ab initio* DFT calculations. Our analysis indicated that a single Ag_{11} cluster can bond with up to 12 O atoms. Moreover, we evidenced that the Ag-O bonds in the nanoclusters include contribution from the Ag 4d states, with a remarkable difference with the case of Ag single crystal surfaces, for which only Ag 5s states are involved. The oxidized $Ag_{11}O_{12}$ nanocluster is indeed more similar to a bulk oxide rather than to an oxidized surface, as it reaches a final hybrid structure formed of d^{10} Ag(I) and d^8 Ag(III) ions which strongly resembles that of AgO bulk oxide. Furthermore, we found that the Ag 3d core level in the Ag_{11} nanoclusters is dominated by initial state effects and has a unique behavior when increasing the oxygen density. This anomaly seems to be related to the dimensionality of the nanocluster and provides an excellent example of the differences that sub-nanometer atomic aggregates of a material show with respect to the bulk and surface counterparts.

11:40am **SS2+AS+HC-WeM-12 Precision Engineering of Metal Nanoparticle Surfaces for Fundamental Studies of Catalytic Reactivity***, **Michelle Personick,*** Wesleyan University **INVITED**

Understanding fundamental structure-activity relationships in catalysis is key to enabling the directed design of improved catalytic materials, but the surfaces of working catalysts are complex. The use of precisely defined nanomaterials provides a powerful tool for facilitating insights into active site structure and reaction mechanisms. Such materials also enable testing and validation of insights from fundamental experimental and computational surface science under catalytic operating conditions. However, synthesizing nanomaterials with the precise surface structures and compositions necessary to test specific hypotheses is a significant challenge, and creative new approaches to materials synthesis are required—particularly for bimetallic materials. This talk will highlight the use of large (~75 nm), well-defined metal nanoparticles as model surfaces to test predictions from computational surface science. In addition, it will describe materials-generalizable synthetic tools developed by our research group for controlling metal nanoparticle shape, surface structure, defect structure, and composition, with an emphasis on dilute bimetallic nanoparticles. Halide-assisted metal ion reduction enables the controlled co-reduction of metals with dissimilar reactivity (Au/Pd, Pd/Cu, Au/Ag), while differentially tuning the relative rates of reduction for each metal to define the shape and surface composition of the material. Plasmon-assisted metal ion reduction takes advantage of the light-responsive properties of materials like Ag to enable (1) the directed deposition of catalytically active but poorly plasmonic metals such as Pt, and (2) the reconfiguration of monometallic Ag materials to modify defect structure while retaining the same surface structure and adsorbates. Together with other techniques developed in our research group, these tools provide a platform for the precision engineering of catalytic metal nanomaterials.

Thin Films Division
Room 317 - Session TF1+SE-WeM
Vapor Deposition and Vapor Infiltration of Organic, Polymeric, and/or Hybrid Materials

Moderator: Siamak Nejati, University of Nebraska-Lincoln

8:00am **TF1+SE-WeM-1 Thermophysical Properties of Organic-Inorganic Hybrid Thin Films Created via Vapor Phase Infiltration (VPI)*, Mark Losego,*** Georgia Institute of Technology

This talk will discuss how thermophysical properties, including the glass transition, thermal expansion, and onset of crystallization, are altered when an organic material is transformed into an organic-inorganic hybrid material via vapor phase infiltration. Vapor phase infiltration (VPI) is a gas-phase technique that exposes organic materials to inorganic vapors (e.g., metalorganics or metal halides) that sorb into the organic, transforming it into an organic-inorganic hybrid. Over the past several years, our lab has examined how the precursor-organic chemistry and VPI process conditions (e.g., temperature) can be used to alter the quantity of inorganic loading and the extent to which the inorganic becomes chemically bound to the organic components. Controlling this physicochemical structure also alters the thermophysical properties of the resultant hybrid material. This talk will describe several examples including altering the glass transition temperature in poly(styrene-co-2-hydroxyethyl methacrylate) (PS-r-PHEMA) random copolymers infiltrated with aluminum oxyhydroxide and in Spiro-OMeTAD hole transport layers infiltrated with titanium oxide. In the PS-r-PHEMA system, random copolymers of varying HEMA composition from 0 to 20 mol% were investigated and the T_g was found to systematically increase with increasing HEMA temperature by as much as 40 °C. Changes in T_{-g} at low HEMA composition, for which the polymer is fully infiltrated, fit the Fox-Flory model for crosslinking phenomena which, in addition to a dissolution study on these materials, suggests that VPI crosslinks the PS-r-PHEMA, raising its glass transition temperature. Interestingly, according to the Fox-Flory model, these cross-links are 5x to 10x stiffer than usually observed for most organic crosslinks, suggesting an interesting phenomenon for inorganic cross-linking. For the Spiro-OMeTAD system, T_g appears to decrease with inorganic infiltration. This result is attributed to a lack of primary bonding between the inorganic and organic phases; the inorganic clusters now serve to disrupt the natural π-π stacking in the Spiro-OMeTAD, lowering T_g. Conversely, though, this disruption of the intermolecular forces leads to an increased resistance to crystallization in these hybrid films. This reduced propensity for crystallization may be useful for improving long-term stability of Spiro-OMeTAD-based organic electronic devices.

8:20am **TF1+SE-WeM-2 Chemical Vapor Deposition of Soft Materials for Garment-Integrated Sensor Systems and Plant Electronics*, Trisha L. Andrew,*** University of Massachusetts Amherst **INVITED**

Chemical vapor deposition is a single-step processing method for forming functional polymer films on unconventional substrates, such as commodity textiles and living plants, and allows fabrication of rugged and sensitive fabric-, fiber- and/or plant-based sensors for wearable electronics and smart farms. I will the detail the materials science and engineering advances made by my team during the process of assembling various garment-integrated sensor systems and plant-based sensors for longitudinal health monitoring in native environments. In particular, I will highlight our recent work in developing garments for portable brain activity monitoring and activity tracking, systems for in-home sleep monitoring, and conductive living plants for detection of selected abiotic stressors in commercial farms.

9:00am **TF1+SE-WeM-4 Effects of Trimethylaluminum Vapor Pressure and Exposure Time on Inorganic Loading in Vapor Phase Infiltrated PIM-1 Polymer Membranes*, Benjamin Jean,*** *Y. Ren, E. McGuinness, R. Lively, M. Losego,* Georgia Institute of Technology

Vapor phase infiltration (VPI) is a process for synthesizing organic-inorganic hybrid materials by infiltrating polymers with inorganic vapor molecules. Recently, our research team has used VPI to synthesize hybrid membranes with consistent nanofiltration performance in a variety of organic solvents that would otherwise swell or dissolve the parent polymer membrane. The properties of these hybrid materials can vary with the amount of VPI generated inorganic loading. However, the relationship between VPI processing conditions and inorganic loading is still not fully understood. This talk will discuss the effects of VPI dose pressure and exposure time on inorganic loading using the technologically relevant membrane material polymer of intrinsic microporosity 1 (PIM-1). At sufficiently low dose pressures and infiltration times (i.e., before saturation), inorganic loading can be controlled with both vapor pressure and exposure time. However, inorganic loading appears to saturate for this system at around 13 wt% inorganic. This apparent saturation point can be reached by infiltrating for 5 hours at TMA dose pressures above 0.4 Torr or after 40 hours at lower vapor pressures of 0.1 Torr. Inorganic loading appears to saturate for this system when the polymer's functional groups become fully populated with bound VPI precursors. These experimental results can be understood with the use of a recently developed reaction-diffusion model for VPI. Critical to applying this model to these post-deposition measurements is re-normalizing the mass loading to the total number of functional groups in the polymer. These findings suggest that the vapor pressure during infiltration affects the kinetics of this infiltration process but does not appear to alter the thermodynamically determined saturation point for inorganic loading.

9:20am **TF1+SE-WeM-5 Elucidating the Sequential Infiltration of Trimethylaluminum and Water Into Polycarbonate Membranes and Thin Films*, Rajesh Pathak,*** *R. Shevate, A. Mane , J. Elam,* Argonne National Laboratory, USA

Sequential infiltration synthesis (SIS) enables the creation of inorganic or polymer-inorganic hybrid nanocomposite materials through the diffusion of metal-organic vapor reagents into polymers and subsequent reactions with the polymer functional groups. Here we report a detailed study of aluminum oxide (Al_2O_3) SIS using trimethyl aluminum (TMA) and H_2O in polycarbonate (PC) thin films and membranes. We employed in situ Fourier transform infrared spectroscopy (FTIR) to elucidate the chemical interactions and in situ spectroscopic ellipsometry (SE) to measure the physical and optical changes that occur during Al_2O_3 SIS in PC. During the first SIS cycle, FTIR measurements revealed a rapid and irreversible reaction between TMA and the PC carbonyl groups to form $Al-CH_3$ species which then converted to Al_2O_3 upon H_2O exposure during.Virtually no spectral changes were observed by FTIR in subsequent SIS cycles.The SE measurements showed that the PC film thickness increased by ~75% and the refractive index (RI) decreased by ~2% during the initial TMA exposure.These effects were partially reversed during the following H_2O exposure such that the net thickness increase was ~36% and the RI returned to its initial value.During subsequent SIS cycles, the thickness and RI remained essentially constant.Ex situ X-ray photoelectron spectroscopy (XPS) depth profiling measurements showed ~30 at% Al uniformly distributed through the depth of the PC film following a single Al_2O_3 SIS cycle. SIS-derived nano/microstructure materials with tunable structural and optoelectronic properties could be developed for a variety of applications.

Keywords: atomic layer deposition; sequential infiltration synthesis; aluminum oxide, polymer-inorganic nanocomposite.

9:40am **TF1+SE-WeM-6 Kinetics of $TiCl_4$ Vapor Phase Infiltration (VPI) into PMMA and the Resulting Thermophysical and Optical Properties of the TiO_2 -PMMA Hybrids*, Shuaib Balogun,*** Georgia Institute of Technology*; A. Steiner,* Sandia National Lab*; M. Losego,* Georgia Institute of Technology

Vapor phase infiltration (VPI) is a post-polymerization modification technique that imbues inorganic materials into polymers to create organic-inorganic hybrid materials with new properties distinct from the parent polymer. While several VPI precursor-polymer chemistries have been explored, a lack of chemical intuition remains for fully understanding the thermodynamics and kinetics that govern the VPI process. This study seeks to continue to build this knowledge by examining the VPI process kinetics for TiO_2 infiltration into PMMA via the use of $TiCl_4$ and H_2O precursors. In this research, polymethylmethacrylate / TiO_2 hybrid materials are prepared using VPI. The depth of infiltration of the TiO_2species into ~200 nm PMMA thin films is studied using x-ray photoelectron spectroscopy (XPS), Fourier-transform infrared (FTIR) spectroscopy and spectroscopic ellipsometry. The kinetics for TiCl4 infiltration increases with both VPI process temperature and $TiCl_4$ exposure time. However, the rates of infiltration are considerably slower than those observed in the more commonly studied trimethylaluminum (TMA) / PMMA system. Even at 150 °C, process times of at least 12 hours are required to fully infiltrate a 200 nm PMMA film whereas using TMA similar films are fully infiltrated within 1 hour at the same process temperature. Films that we believe to be fully infiltrated at 150 °C and 24 hours of $TiCl_4$ exposure have a 6 at% Ti in the innermost bulk, as determined by XPS. Interestingly, unlike AlO_x-PMMA hybrids, these TiO_x – PMMA hybrids exhibit significant changes in their optical properties. Increased titanium loading leads to a 4% increase in refractive index and increased UV absorbance in the UV range of 270-350nm. Furthermore, films infiltrated at 150 °C and 24 hours of $TiCl_4$ exposure had a 50 % and 70 % reduction in coefficients of thermal expansion (CTE) below and above T_g respectively. Reduced CTE trends with increased titanium loading. We will discuss possible opportunities to use these new properties for various applications.

This project is supported by the Laboratory Directed Research and Development program at Sandia National Laboratories, a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia LLC, a wholly owned subsidiary of Honeywell International Inc. for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

11:20am **TF1+SE-WeM-11 Effect of the Metal-Heteroatom Bond on Film Growth and Properties in Vapor-Deposited, Hybrid Metal Organic Thin Films**, ***Jacqueline Lewis***, *J. Shi, A. Ravi, S. I-Cheng Hsu, S. Bent,* Stanford University

Growing energy demand and the transition to clean energy set the stage for novel materials to fill gaps in current technologies. Hybrid metal organic thin films allow useful, active materials in the energy field, such as Al2O3 and ZnS, to reach a wider range of functionality by adding organic linkers via molecular layer deposition (MLD). Varying the organic linker and metal center using MLD modifies the film properties significantly, giving an adaptable, layer-by-layer growth scheme for the formation of novel materials. Previous literature reports have mainly focused on metal alkoxide films, where the organic linker is a multifunctional organic alcohol. Typically using a bifunctional linker, these films degrade rapidly in air, limiting their potential applicability for membrane materials, catalysis, and encapsulation. However, different functional groups, including dithiols, change the film properties substantially, with stability in air as one of the most notable effects. In this work, zinc thiolate films were deposited via hybrid MLD with a thiol bonding group, showing increased air stability as the films retain ~60% of the thiolate character after over 6 weeks in air. Films grown using 1,2-ethanedithiol degrade faster than those grown with 1,4-butanedithiol. The degradation mechanism forms at least three separate species, which we study via X-ray photoelectron spectroscopy (XPS) and synchtrotron-based X-ray absorption spectroscopy (XAS). Despite some degradation observed via XPS, the band gap of the material stays consistently close to 5.0 eV assuming direct band gap. This multi-week decay is much slower than the degradation of the known metal alkoxides, which degrade on the timescale of hours or days. The increased functionality exhibited by these metal thiolate films shows that changing the metal-heteroatom bond can create more stable films as well as increase the domain of materials to examine.

11:40am **TF1+SE-WeM-12 Oxidative Molecular Layer Deposition of Electrochemically Active Polymers**, ***Matthias Young***[1], *Q. Wyatt, M. Vaninger, N. Paranamana, T. Heitmann, H. Kaiser,* University of Missouri

Conjugated polymers such as polyethylenedioxythiophene (pEDOT), polypyrrole (pPy), and polyaniline (pAni) exhibit high electrochemical capacities, making them appealing as electrode materials for energy storage, electrochemical desalination, and chemical sensing. Recent work has established the growth of thin-films of pEDOT using alternating gas-phase exposures of EDOT monomers and a metal-chloride (e.g. $MoCl_5$) oxidant in a process termed oxidative molecular layer deposition (oMLD). Here, we report on recent work establishing oMLD of amine-containing conjugated polymers. We find that pyrrole (Py) and $MoCl_5$ undergo self-limiting surface reactions during oMLD exposures to form conformal pPy thin films, but oMLD using aniline (Ani) and p-phenylenediamine (PDA) monomers yield unexpected azo functionality. The formation of azo groups is attributed to an $MoCl_5$-amine surface adduct that spatially constrains polymerization reactions near the amine group and produces azo groups when coupling two primary amines. pPy grown by oMLD exhibits a record-breaking 282 mAh/g capacity in aqueous electrolyte, and PDA/$MoCl_5$ oMLD yields azo-polymers of interest as anode materials for alkali-ion batteries. Alternating between Py and PDA monomers during oMLD produces molecularly mixed copolymers with qualitatively different electrochemical responses from the isolated monomer structures. This work lays the foundation for the growth of conformal thin films of conjugated amine polymers with molecular-level control of composition and thickness.

12:00pm **TF1+SE-WeM-13 Towards High Throughput Molecular Layer Deposition of Alucone Films**, ***Hardik Shantilal Jain***[2], Holst Centre / TNO and Eindhoven University of Technology, The Netherlands; *M. Creatore,* Eindhoven University of Technology, The Netherlands; *P. Poodt,* Holst Centre / TNO and Eindhoven University of Technology, The Netherlands

The deposition rate and properties of MLD films are for a large part determined by what happens during the precursor exposure step. In some cases, however, the purge step is of equal importance, for example in the MLD of alucone films using trimethylaluminum (TMA) and ethylene glycol (EG). Due to the porosity of alucone films, the reactants during their exposure step not only react at the film surface but also tend to infiltrate into the film. The subsequent outgassing of the infiltrated reactant can take relatively very long thereby becoming the deposition rate-limiting step. If enough purge time is not provided for the reactant to outgas, it will lead to an additional CVD component alongside MLD in the overall growth. To employ/avoid the CVD component in the deposition process, we have developed a kinetic model to correlate parameters like exposure times, partial pressures, purge times and deposition temperature to the amount of CVD component in the growth. We have also investigated the impact of this additional CVD component on the step coverage of the alucone films and evaluated its usage in superconformally filling dielectric gaps.

Additionally, we also looked into solutions to increase the deposition rate of the alucone films and improve their conformality and amongst others found that using a bulkier precursor like DMAI instead of TMA can overcome the problem of precursor infiltration, increase the deposition rate of alucone processes by at least an order of magnitude and provide quite conformal films. We also performed a detailed investigation of MLD of alucone using DMAI as the aluminum precursor wherein the effect of deposition temperature and reactant purge times on deposition kinetics has been investigated and the DMAI alucone films have been compared with those prepared using TMA for their chemical environment and degradation showing striking similarities between both. We believe that the above work could be extended to other MLD systems and can serve as a guide in designing efficient MLD reactors and processes.

Thin Films Division
Room 316 - Session TF2+AP+SE+SS-WeM
ALD and CVD: Surface Reactions, Mechanisms and Kinetics

Moderator: Jessica Kachian, Intel Corporation

8:00am **TF2+AP+SE+SS-WeM-1 Nucleation Enhancement of Ruthenium Atomic Layer Deposition Using Organometallic Molecules**, ***Amnon Rothman***, *D. Tsousis, S. Bent,* Stanford University

Atomic layer deposition (ALD) is an attractive surface-sensitive thin-film deposition technique used in advanced technologies such as microelectronics, catalysis, and energy applications. The self-limiting surface reactions during the ALD process promote the layer-by-layer growth mechanism, thus providing significant control over the film thickness and conformality. However, due to an island growth mechanism and nanoparticle formation, metal ALD on oxide surfaces can lead to poor-qualify films and display long nucleation delays. One of the main reasons for the nucleation delays can be attributed to the differences in the surface energy between metals and oxide surfaces. In this work, we study the nucleation enhancement of ALD ruthenium layers on Si substrates by using a single monolayer of trimethylaluminum (TMA) or diethylzinc (DEZ) preadsorbed on the substrate prior to deposition. The nucleation enhancement is demonstrated for ruthenium ALD using two different ALD precursors, cyclopentadienylethyl(dicarbonyl)ruthenium(II) (RuCpEt(CO)2) and bis(cyclopentadienyl)ruthenium(II) (RuCp2), with O2 as a counter reactant. The ruthenium ALD nucleation and growth mechanism were studied using scanning electron microscopy (SEM), ellipsometry and X-ray photoelectron spectroscopy (XPS), both on the treated and untreated substrates. The results show that pretreatments using organometallic molecules reduce the nucleation delay of the ruthenium layer. The surface pretreatment strongly influences the ruthenium nucleation, yielding up to a 1.5-fold and a 2.1-fold increase in the surface coverage of the metal while using RuCpEt(CO)2 and RuCp2, respectively. Interestingly, pulsing TMA or DEZ, with or without exposure to H2O, is equally effective. We hypothesize that the high coverage in the pretreated samples is attributed to an increase in the substrate's surface energy, enhancing the surface diffusion of nanoparticles and adatoms during growth. We confirm that exposure of

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[1] **2020 TFD Paul Holloway Awardee**

[2] **TFD James Harper Award Finalist**

organometallic molecules during ruthenium ALD using the precursors above introduces a potential pathway toward achieving high-quality ruthenium thin films.

8:20am **TF2+AP+SE+SS-WeM-2 Ald of Chalcogenide and III-V Materials for Memory Applications**, ***Laura Nyns****, A. Delabie, W. Devulder,* IMEC, Belgium; *J. Girard,* Air Liquide, France; *B. McKeown, V. Pallem,* Air Liquide; *T. Peissker, J. Sinha,* IMEC, Belgium; *N. Stafford,* Air Liquide; *J. Swerts,* IMEC, Belgium **INVITED**

To enable fast and powerful storage solutions for next generation mobile applications and other innovative technologies, the memory landscape focuses on various concepts. These concepts include DRAM for high-speed access, NAND flash memory for storage of large amounts of data, and the emerging Storage Class Memories (SCM) for massive data access in short time. Each of these technologies require their own set of materials with specific characteristics. Additionally, material deposition can be challenging because of the high aspect ratios which are typical for these advanced 3D architectures. Atomic Layer Deposition (ALD) has been shown to be a promising technique in that respect, as conformal deposition of a wide range of materials in complex topographies was established over the past decades. In this talk, we will address the ALD of germanium chalcogenides, a class of materials which is being explored as phase change memory and selector elements for SCM applications. GaAs will also be discussed, due to the need for high mobility channel materials to replace poly-Si in NAND flash technologies. We used the dechlorosilylation chemistry for the ALD of chalcogenide and III-V materials, where (nonmetal) alkylsilyl compounds react with metal chlorides to enable the growth of amorphous layers at low deposition temperatures [1]. An ALD GaAs process could be established, resulting in smooth and stoichiometric films that are amorphous as deposited. Crystallization into the preferred cubic phase was obtained at 350-400˚C, despite the presence of a Ga-rich surface oxide due to air exposure. Irrespective of the excellent step coverage in high aspect ratio structures, we found that these films are prone to delamination. We encountered a comparable challenge with ALD GeSe and $Ge_2Sb_2Te_5$ (GST) using this chemistry, and could demonstrate the benefit of proper surface treatments prior to film deposition to engineer the interface structure and improve layer adhesion. For GeSe, the extension of the existing ALD process [2] to ternary and even quaternary compounds is needed to boost the memory cell performance. We will therefore report on the development of an ALD process targeting GeAsSe deposition. Finally, we explored area-selective deposition (ASD) of chalcogenide materials, as this could greatly simplify the fabrication of complex 3D SCM devices. Our results indicate an impressive selectivity of 96% for GST films of ~22nm on TiN compared to SiO_2, by using the dechlorosilylation chemistry in combination with a dimethylamino-trimethylsilane (DMA-TMS) surface treatment.

[1] Pore et al, ***J. Am. Chem. Soc.***, 2009, **131**, 3478-3480

[2] Haider et al, ***Mater. Adv.***, 2021,**2**, 1635-1643

9:00am **TF2+AP+SE+SS-WeM-4 Plasma-enhanced Spatial ALD of SiO_2 investigated by gas-phase Infrared and Optical Emission Spectroscopy**, *M. Mione, V. Vandalon,* Eindhoven University of Technology, Netherlands; *A. Mameli,* TNO-Holst Centre & Eindhoven University of Technology, The Netherlands; *F. Roozeboom,* TNO-Holst Centre & Eindhoven University of Technology, Netherlands; ***Erwin Kessels,*** Eindhoven University of Technology, Netherlands

A spatial atomic layer deposition (ALD) process for SiO_2 using bisdiethylaminosilane (BDEAS, $SiH_2[N(C_2H_5)_2]_2$) and an atmospheric O_2 plasma is reported as well as an investigation of its underlying reaction mechanisms [1]. Within the substrate temperature range of 100-250 ᵒC, the process demonstrates self-limiting growth with a growth-per-cycle between 0.12 and 0.14 nm and SiO_{-2} films exhibiting material properties *on par* with those reported for low-pressure plasma-enhanced ALD (PEALD) [2].

Gas-phase infrared spectroscopy on the reactant exhaust gases and optical emission spectroscopy on the plasma region are used to identify the species that are generated in the ALD process. Based on the identified species and a calibration procedure, we propose a reaction mechanism where BDEAS molecules adsorb on –OH surface sites through the exchange of one of the amine-ligands upon desorption of diethylamine (DEA, $HN(C_2H_5)_2$). The remaining amine ligand is removed through combustion reactions activated by the O_2 plasma species leading to the release of H_2O, CO_2, CO in addition to products such as N_2O, NO_2, and CH-containing species. These volatile species can undergo further gas-phase reactions in the plasma as indicated by the observation of OH*, CN* and NH* excited fragments in emission. Furthermore, the infrared analysis of the precursor exhaust gas indicated the release of CO_2 during precursor adsorption. Moreover, this analysis has allowed the quantification of the precursor depletion yielding values between 10 % and 50 % depending on the processing parameters. On the basis of these results, the overall surface chemistry of the spatial ALD process of SiO_2 will be discussed.

[1] M. Mione, V. Vandalon, A. Mameli, W.M.M. Kessels, and F. Roozeboom, J. Phys. Chem. C 125, 24945 (2021)

[2] G. Dingemans, C.A.A. van Helvoirt, D. Pierreux, W. Keuning, W.M.M. Kessels, J. Electrochem. Soc. 159, H277 (2012)

9:20am **TF2+AP+SE+SS-WeM-5 Role of Al in Enhancing Growth Rate and Crystallinity in Chemical Vapor Deposition of $Hf_{1-x}Al_xB_2$ Coatings Below 300 °C**, ***Kinsey Canova***[1], *S. Shrivastav, C. Caroff, L. Souqui, G. Girolami, J. Krogstad, J. Abelson,* University of Illinois at Urbana-Champaign

Transition metal diborides are desirable as hard, low-friction, and wear-resistant coatings for applications in extreme environments. To survive high temperatures, the coatings must have a very low rate of microstructural evolution and must resist oxidation, in particular the loss of boron via evaporation of boron oxide. We previously showed that amorphous HfB_2 films can be deposited by chemical vapor deposition (CVD) using a borohydride precursor, $Hf(BH_4)_4$. However, at T > 600 °C, those coatings crystallize and densify, which leads to cracking, and they oxidize readily. Here, we co-flow an aluminum precursor, trimethylamine alane (TMAA), to deposit ternary $Hf_{1-x}Al_xB_2$ alloy films by CVD at temperatures ≤ 300 °C. This affords excellent film deposition and properties: (i) Al incorporation substantially increases the reaction rate of the HfB_2 precursor, yet the growth still gives good conformal coverage over all surfaces in deep features. (ii) The as-deposited films are nanocrystalline, and the lattice parameters are consistent with a random alloy on the metal sublattice, as opposed to a mixture of HfB_2 and AlB_2 grains. (iii) No elemental Al is detected, so there is not a mechanically soft, low-melting phase. (iv) Annealing films to 700 °C in air creates an Al_2O_3 surface layer that protects the underlying film, and negligible grain growth is observed. To determine a cause of the enhanced growth rate, we performed a matrix of growth experiments vs. precursor pressures and temperature; the Al incorporation rate, which is proportional to TMAA flux, has the strongest effect on rates. We hypothesize that Al consumes the excess boron from the HfB_2 precursor – which contains four boron atoms for every Hf atom – and forms AlB_2. This overcomes the probable rate limiting step of HfB_2 deposition, i.e., the associative desorption of excess boron from the growth surface as B_2H_6, and it is consistent with the improved film crystallinity. Finally, this study provides a guide to the parameters controlling growth rate and composition.

9:40am **TF2+AP+SE+SS-WeM-6 Pushing the Limits of ALD Infilling to Produce Macroscopic Nanocomposites**, ***Benjamin Greenberg****, K. Anderson, A. Jacobs, J. Wollmershauser, B. Feigelson,* U.S. Naval Research Laboratory

Atomic layer deposition (ALD) infilling is a reliable and popular technique for producing nanocomposite thin films. Typically, ALD precursor dose times on the order of 1 s are sufficient for infiltrating and conformally coating the pores of nanoparticle (NP) networks with thickness on the order of 1 µm or less. In principle, the application space for this nanocomposite production method could be expanded significantly by increasing the NP network thickness to 1 mm or greater. In this work, we investigate the possibility of achieving this scale-up through increasing the ALD precursor dose time by three orders of magnitude. We hydraulically press aluminum oxide nanopowder with particle size on the order of 100 nm to form nanoporous compacts with ~2 mm thickness and ~50% solid volume fraction, and we coat the pores with either Al_2O_3 or ZnO by static-dose ALD, holding precursor vapor in the ALD chamber for >1,000 s per half-cycle. For both coatings, we analyze the ALD chamber pressure traces to understand precursor diffusion and reaction kinetics, and we compare our results to predictions based on a Knudsen diffusion model. For the ZnO coating, we use electrical conductivity measurements, X-ray crystallography, scanning electron microscopy, and energy-dispersive X-ray spectroscopy to evaluate coating composition and uniformity within the nanocomposite, and we compare the ZnO-infilled-Al_2O_3 nanocomposite to a compact of core/shell Al_2O_3/ZnO NPs produced by particle ALD (pALD) in a rotary reactor. Preliminary data suggest that uniform infilling of a macroscopic NP network is possible provided that it can be carried out at a temperature sufficiently low to prevent precursor decomposition.

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[1] **TFD James Harper Award Finalist**

Thin Films Division
Room 316 - Session TF3+MS-WeM
Simulations and Machine Learning Applications for Thin Films

Moderator: Angel Yanguas-Gil, Argonne National Lab

11:00am **TF3+MS-WeM-10 What an Experimentalist Needs from Computational Materials Science (Including Machine Learning) – Studies in Semiconductor Processing and Metrology***, **Rafael Jaramillo**,* MIT **INVITED**

I will present a view on computational materials science and machine learning, from the perspective of an experimentalist working primarily on compound semiconductors. I will first present uses of computation within my own group. These include computational thermodynamics to guide materials design and synthesis, atomistic modeling of deep levels in semiconductors, finite-element modeling of mechanical and acoustic phenomena, and machine learning models of optical metrology to improve materials discovery and microelectronics manufacturing. In many cases, our computations are limited by challenges that are beyond our expertise as experimentalists. With these challenges in mind, I will then highlight several outstanding needs from the computational science community, illustrated by ongoing research projects:

(1) We pioneered the synthesis of chalcogenide perovskite thin films by gas-source molecular beam epitaxy (MBE). Our successes pose questions of process optimization, particularly related to connections between precursor selection, processing temperature, and crystal quality. There is a need for multi-scale modeling of crystallization at solid-vapor interfaces, including highly-non-thermodynamic conditions such as plasma processing, to de-risk the development of manufacturing-compatible deposition methods.

(2) We discovered that chalcogenide perovskites have the strongest low-frequency dielectric response among VIS-NIR semiconductors. The only other family of semiconductors with comparable dielectric response are halide perovskites. We also discovered that chalcogenide perovskites have, in common with their halide cousins, slow non-radiative excited-state recombination. These observations pose the question of how, exactly, soft phonon spectra affect Schottky-Read-Hall (SRH) recombination rates. Polarons may be relevant. Exact calculations of SRH capture cross sections for particular materials, coupled to a Fröhlich model of electron-phonon interactions, would shed light on these open questions in solar cell materials physics.

(3) Native oxidation of chalcogenide layered and two-dimensional semiconductors (notably including transition metal dichalcogenides, TMDs) needs to be well understood for microelectronics fabrication, and presents unique opportunities for ultra-scaled logic and memory devices. We have used theory and experiment to describe TMD native oxidation processes. However, reactive molecular dynamics simulations combined with advanced data analytics are needed to accelerate progress towards device technology that would be advanced and manufacturable.

11:40am **TF3+MS-WeM-12 Computational Analysis and Design of Precursors for ALD and CVD of Metals***, S. Elliott, A. Chandrasekaran, S. Tiwari, A. Fonari, D. Giesen,* Schrödinger*; **Casey Brock**,* Schrödinger

Understanding a deposition process depends to a large extent on understanding the chemical and physical properties of the precursor molecules. Volatility, reactivity and thermal stability are the three key precursor characteristics needed for chemical vapor deposition (CVD) and atomic layer deposition (ALD), although properties such as melting point, viscosity, synthetic cost and nucleation behavior are also important. Quantifying these characteristics for known precursors can help trouble-shoot an existing process, and designing novel precursors with optimum characteristics is a robust way to improve a process. We illustrate these points on the example of beta-diketonate-based Pd(II) precursors for the deposition of palladium metal. The aim is to find the optimum ligand combination in both homoleptic and heteroleptic complexes.

Precursor volatility often dictates the lower limits of temperature and pressure at which a process can be run. We use a machine-learning model of volatility to see the effect of ligand identity on this property. Specifically, cyclopentadienyl and allyl ligands are found to lower the evaporation temperature to <100 degrees C in the 1-5 Torr pressure range. The other end of the process window is determined by thermal decomposition. For Pd(hfac)2 and formalin experiments show a narrow ALD window between 200 and 230°C, followed by decomposition at higher temperatures. We therefore use density functional theory (DFT) to assess the thermal stability of candidate complexes. We exclude those heteroleptic complexes that DFT predicts to be impossible to synthesize because of ligand exchange. We find that the poor stability of thd complexes can be overcome by switching to fluorinated ligands. We also present quick and approximate measures of the reactivity towards reduction to metallic Pd, whether by CVD or ALD, and compare these with more time-consuming DFT calculations of the surface chemistry.

The computational tools for these properties have been automated to the level where they can be integrated into a team's R&D workflow for routinely assessing current precursors or discussing new ones, so that lists of molecules can be generated and ranked according to the key characteristics for a particular process and application area.

12:00pm **TF3+MS-WeM-13 Dopant-selective Atomic Layer Deposition of Metals for Bottom-up Nanoelectronics***, **Nishant Deshmukh**,* Georgia Institute of Technology, USA*; D. Aziz, A. Brummer, M. Filler,* Georgia Institute of Technology

The entirely bottom-up fabrication of nanoelectronic devices promises electronics with an unprecedented combination of performance and scalability. A long-standing challenge has been the bottom-up fabrication of nanoscale features on nanoscale semiconductors. Bottom-up methods can create suitable semiconductor structures, but top-down methods are needed for other important device features, such as contacts or gate stacks. For example, Si nanowire pn diodes can be readily fabricated with the vapor-liquid-solid (VLS) growth method; however, lithography is still necessary to define contacts to the p and n segments. Here, we report a dopant-selective atomic layer deposition (ALD) process to deposit metal thin films suitable for constructing fully bottom-up pn diodes. Briefly, undecylenic acid, a bifunctional self-assembled monolayer (SAM), is blanket attached to the Si surface. Exposure to KOH removes it from the surface of heavily-doped (~10^{20} cm^{-3}) p-type and n-type Si while it remains on lightly-doped (~10^{14} cm^{-3}) Si. Subsequent Pt ALD yields deposition only on the heavily-doped Si. X-ray photoelectron spectroscopy (XPS) shows that the ratio of Pt deposition on the heavily-doped to lightly-doped Si can be as high as 130. We suspect that this high selectivity results from undecylenic acid attaching to lightly-doped Si through its alkene group, and to heavily-doped Si through its carboxylic acid group. This difference in attachment results in KOH being able to remove undecylenic acid only from the heavily-doped Si, thus allowing Pt to deposit.

2D Materials Technical Group

Room 303 - Session 2D+EM+MI-WeA

2D Materials: Charge Density Waves, Magnetism, and Superconductivity

Moderators: An-Ping Li, Oak Ridge National Laboratory, **Xiaomeng Liu**, Princeton University

2:20pm **2D+EM+MI-WeA-1 Tunable Electronic Structure and Correlations in Quasi-Freestanding Monolayer Transition Metal Disulfides*, Thomas Michely,*** Universität zu Köln, Germany **INVITED**

In situ reactive molecular beam epitaxy using single crystal graphene as a substrate enables to grow transition metal disulfides as quasi-free standing monolayers under well controlled conditions. Thereby access to their undisturbed electronic properties of as well as to those of their intrinsic defects is provided.

A non-invasive technique to shift the chemical potential in semiconducting transition metal disulfide layers like MoS_2 or WS_2 through p- and n-type doping of graphene is presented, while graphene remains a well-decoupled 2D substrate. These shifts induce giant band gap renormalizations, insulator-to-metal to insulator transitions and affects the metallic states in mirror twin boundaries.

Electronic correlations are known to be strong for dimensional reasons in transition metal dichalcogenide monolayers and often give rise to charge density waves and other competing electronic phases. The dependence of charge density waves on the environment and its layer dependence are investigated for several transition metal disulfides. We show that monolayers of VS_2 realize a CDW which stands out of our expectations. It displays a full CDW gap residing in the unoccupied states of monolayer VS_2 and the CDW induces a topological metal-metal (Lifshitz) transition. Non-linear coupling of transverse and longitudinal phonons is essential for the formation of the CDW and the full gap above the Fermi level.

Lastly we will focus to mirror twin boundaries in MoS_2 and investigate how to determine quantized polarization charges on these domain boundaries, whether they are subject to Fermi level pinning and how shifts in the Fermi level change screening of their line charge.

Contributions to this work by Clifford Murray, Camiel van Efferen, Wouter Jolie, Jeison Fischer, Timo Knispel, Joshua Hall, Stefan Kraus, Felix Huttmann, Carsten Busse, Niels Ehlen, Boris Senkovskiy, Martin Hell, Alexander Grüneis, Hannu-Pekka Komsa, Arkady Krasheninnikov, Jan Berges, Erik van Loon, Arne Schobert, Malte Rösner, Tim Wehling, Nico Rothenbach, Katharina Ollefs, Lucas Machado Arruda, Nick Brookes, Gunnar Schönhoff, Kurt Kummer, Heiko Wende, Philipp Weiß, Fabian Portner, and Achim Rosch are gratefully acknowledged.

3:00pm **2D+EM+MI-WeA-3 Dopants Modulated Interplay of Charge Density Wave and Superconductivity in 2D VdW Layered ZrTe3*, Xiao Tong,*** . Center of Functional Nanomaterials, Brookhaven National Laboratory*; Y. Liu, Z. Hu,* Condensed Matter Physics and Materials Science Department, Brookhaven National Laboratory*; D. Leshchev,* National Synchrotron Light Source II, Brookhaven National Laboratory*; X. Zhu, H. Lei,* Condensed Matter Physics and Materials Science Department, Brookhaven National Laboratory*; E. Stavitski, K. Attenkofer,* National Synchrotron Light Source II, Brookhaven National Laboratory*; C. Petrovic,* Condensed Matter Physics and Materials Science, Department, Brookhaven National Laboratory

Two-dimensional transition metal trichalcogenides ZrTe3 holds atomic chains in the crystal structure give rise to quasi one-dimensional (quasi 1D) conduction, and features the charge density wav (CDW) below TCDW ¼ 63 K and filamentary superconductivity below 2 K, Here, we report that superconductivity(SC) is enhanced as the consequence of suppressed CDW for Hf dopped ZrTe3, in contrast, SC is suppressed as the consequence of enhanced CDW for the Se dopped ZrTe. Our XPS and Raman studies suggested the suppressed CDW is due to Hf caused disorder in Te2-Te3 atomic chains, while the enhanced CDW is due to Se induced enhanced electron-phonon coupling in unperturbed periodicity of the Te2-Te3 chains, respectively.

3:20pm **2D+EM+MI-WeA-4 Magnetic Order in a Coherent Kondo Lattice in 1T/1H $TaSe_2$ Heterostructures***, W. Wan,* ***Rishav Harsh****, P. Dreher, S. Sajan,* Donostia International Physics Center , Spain*; A. Menino, I. Errea,* Centro de Física de Materiales (CSIC-UPV-EHU), Spain*; F. de Juan, M. Ugeda,* Donostia International Physics Center , Spain

Kondo lattice systems are of fundamental importance for our understanding of quantum criticality and unconventional superconductivity. At the heart of their complexity lies the competition between the opposing forces of Kondo screening and magnetic interactions, which is revealed at very low temperatures as the moments start behaving coherently and eventually determines the fate of the ground state. While our understanding of Kondo lattices has traditionally relied on technically challenging strongly correlated bulk f-electron systems, new light is being shed on the problem thanks to heterostructures of 2D transition metal dichalcogenides, which realize a tunable Kondo lattice platform in a simple material. Here, we study the 1T/1H-$TaSe_2$ heterostructure by high-resolution Scanning Tunneling Spectroscopy at 300 mK, and show a well resolved splitting of the Kondo peak, which increases monotonically in a nonlinear fashion in the presence of an out-of-plane magnetic field. This behavior is unexpected for a fully screened Kondo lattice, and it originates instead from a ground state with residual magnetic order, consistent with a Kondo coupling much below the critical point in the Doniach phase diagram.

4:20pm **2D+EM+MI-WeA-7 Structural and Magnetic Properties of Ultrathin $Cr_{(1+\delta)}Te_2$ Films Grown by Van Der Waals Epitaxy***, Kinga Lasek,*** *P. Coelho,* University of South Florida*; P. Gargiani , M. Valvidares,* ALBA Synchrotron Light Source, Spain*; K. Mohseni , H. Meyerheim , I. Kostanovskiy,* Max Planck Institute of Microstructure Physics, Germany*; K. Zberecki,* Warsaw University of Technology, Poland*; M. Batzill,* University of South Florida

Over the past years, researchers have proved that the layered structure of transition metal dichalcogenides (TMDs) enables the synthesis of novel materials. Specifically, introducing extra transition metal atoms into the vdW gap of the TMDs host lattice leads to various structural, electrical, and magnetic properties modulations. Exploring the latter, in particular, aligns with a recent search for ferromagnetic 2D materials.

In this talk, we will explore the epitaxial growth, structural, surface, and magnetic properties of a bi- to few-layer thick $Cr_{(1+\delta)}Te_2$ ($0 < \delta < 1$)films that represent a group of self-intercalated TMDs materials. These materials demonstratewell-known ferromagnetic ordering and exist in different compositional phases that vary by the amount of Cr intercalated (δ) between $CrTe_2$ layers.By detailed compositional and structural characterization, using scanning tunneling microscopy (STM), and high-resolution Rutherford backscattering (HR-RBS) we will show that the amount of self-intercalated Cr atoms can be controlled by post-growth annealing. Such modified films are characterized by an increased T_c up to 190K, a coercive field being reduced from 0.5 T to 0.3 T, and an isotropization of the magnetic anisotropy confirmed by XMCD measurements.

Finally, we will demonstrate that ultrathin vdW films can be prepared with the ultimate limit of a single self-intercalated layer by vdW epitaxy. These vdW materials maintain their ferromagnetic properties with desirable out-of-plane anisotropy and thus are potential ferromagnetic 2D materials that can be combined in vdW heterostructures by a bottom-up growth process.

4:40pm **2D+EM+MI-WeA-8 Transition Metal Silicates as a Platform for Robust Single Layer, Two-Dimensional Ferromagnetism***, Nassar Doudin,*** *K. Saritas,* Yale University*; P. Shafer, A. T. N'Diaye,* Lawrence Berkeley National Laboratory (LBNL)*; S. Ismail-Beigi, E. Altman,* Yale University

Two-dimensional (2D) materials have received extensive attention and rapid development since the discovery of graphene in 2004.[1] Magnetism in two dimensions has long been at the heart of theoretical, experimental, and technological advances, where great efforts have been made to realize magnetism in 2D materials.[2] To date, 2D magnetic materials have been obtained via exfoliation from bulk samples; however, this makes it difficult to precisely control the thickness and domain size of the samples. Moreover, the most intensely studied 2D magnetic materials (e.g. CrI_3, $Cr_2Ge_2Te_6$) are unstable in air and are only ferromagnetic below ~50 K. Hence, exploring new 2D magnetic materials is of grand significance. Recently, vdW epitaxy techniques have fulfilled the growth of 2D vdW materials on metal substrates, such as 2D silica bilayers and related transition metal silicates which break inversion symmetry guaranteeing at least a piezoelectric response. The arrival of these 2D vdW materials opens up exciting opportunities for preparing 2D multiferroic materials. In this talk, we demonstrate air stable, single layer 2D $M_xSi_2O_5(OH)_y$ (M= Fe, Cr) structures consisting of a silica-capped metal oxide grown on Pd and Au substrates that exhibit ferromagnetic order at room temperature as measured by x-ray magnetic circular dichroism (XMCD) spectroscopy. Application of small magnetic fields proves that the observed magnetic structures follow a hysteretic behavior. SQUID magnetometry confirms these results and reveals high spin-polarization at room temperature with in-plane magnetic anisotropy. The measurements are further supported by first-principles theoretical calculations which highlight approaches to stabilize the magnetic order. Thus $M_xSi_2O_5(OH)_y$ based 2D materials represent a new platform for single layer 2D ferromagnetism with potential multiferroic behavior.

40. Meyer, J. C. *et al.* The structure of suspended graphene sheets. *Nature***446**, 60–63 (2007).
41. K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. G. and A. A. F. Electric Field Effect in Atomically Thin Carbon Films. *Science.***306**, 666–669 (2004).

5:00pm **2D+EM+MI-WeA-9 Novel Materials for Quantum Computing Devices: Monolayer Topological Superconductors*, Yi-Ting Hsu,*** University of Notre Dame **INVITED**

Atomically thin superconductors that possess 'topological properties' have attracted extensive attention since many of them are predicted to host exotic zero-energy quasi-particles called Majorana zero modes (MZMs). MZMs are proposed to be the building blocks in a type of fault-tolerant quantum computation scheme known as topological quantum computation (TQC). One of the pressing challenges in the field of TQC is to experimentally realize such a superconducting film and detect the existence of MZMs. In this talk, I will first discuss what a topological superconductor is and why it is a promising platform for a TQC device. I will then talk about candidate materials in the family of transition metal dichalcogenides. Finally, I will discuss our theory-experiment combined effort to systematically identify more candidates in two-dimensional material databases.

5:40pm **2D+EM+MI-WeA-11 Tuning Magnetism and Superconductivity in Single Layer FeSeTe by Chemical Pressure*, Basu Oli,*** *Q. Zou, H. Zhang,* West Virginia University*; T. Shishidou, M. Weinert,* University of Wisconsin, Millwaukie*; L. Li,* West Virginia University

The interplay of topology, magnetism, and superconductivity in a single-layer FeX (X = S, Se, Te) epitaxially grown on $SrTiO_3$ (STO) substrate provides a model system for investigating a wide range of quantum phenomena. This work explores the impact of chemical pressure on magnetism and superconductivity in single-layer $FeSe_{1-x}Te_x$/STO grown by molecular beam epitaxy using *in-situ* angle-resolved photoemission spectroscopy and scanning tunneling microscopy/spectroscopy. We find that the Fermi surface consists of only an electron pocket at the M point, which decreases in size with increasing Te concentration and disappears completely for $x > 0.75$. At the Γ point, a hole pocket appears with $x > 0.65$, while the bands changes from parabolic to linear up to $x = 0.9$, where it reverts back to parabolic. Accompanying the changes in the band structure, the top of bands at the Γ also shift towards and then away from the Fermi level, indicative of a topological phase transition in $FeSe_{1-x}Te_x$/STO. At 4.3 K, while the FeTe films are non-superconducting, dI/dV tunneling spectra indicate the emergence of superconductivity when Se concentration is greater than 25%. Our spin spiral calculations indicate that the FeTe system exhibits long-range bi-collinear antiferromagnetic (AFM) order, which is tuned toward the checkerboard (CB) AFM fluctuations with the incorporation of Se. Our findings indicate that CB AFM fluctuations are critical for superconductivity in epitaxial single layer iron chalcogenide superconductors on STO.

This research is supported by DOE (DE-SC0017632).

6:00pm **2D+EM+MI-WeA-12 Peculiar Near-Contact Regime of Andreev Reflection at the Breakdown of a Tunnel Junction*, Petro Maksymovych,*** *S. Song,* Oak Ridge National Laboratory*; J. Lado,* Aalto University, Finland*; W. Ko,* Oak Ridge National Laboratory

Recently we introduced non-contact Andreev reflection (NCAR) - a new experimental approach to quantify Andreev reflection in a tunable tunnel junction [1]. The technique utilizes the fundamental connection between the physics of the scattering process and the strength of exponential non-linearity of the tunneling current, and therefore adopts the tunneling current decay rate as the observable. NCAR simultaneously achieves spectroscopy of quasiparticle density of states, atomic-scale resolution and quantitative Andreev reflection, while avoiding the necessity to form invasive and mesoscale mechanical contacts.

One surprising observation of NCAR is that Andreev reflection does not have a monotonous dependence on tip-sample separation. In particular, the decay rate signature of Andreev reflection proceeds through a maximum just before the mechanical contact. In this talk, we will explore in detail the origin of this near-contact regime and its significance for the characterization of superconductivity. In particular, we will rationalize the observations within the accepted BKT model as well as accurate tight-binding simulations, revealing the fundamental connection between the tunneling barrier dependence of Andreev reflection and the order in perturbation theory responsible for the tunneling current. Furthermore, we will highlight the importance of higher order Andreev reflection for the measurement of unconventional superconductors. In general, tunneling and near-contact regimes will qualitatively differ from each other in the case of unconventional superconducting order parameters, enabling direct inference of their symmetry.

At the same time, we will demonstrate how quantitative comparison of statistical distributions of decay rate enables a complementary, probabilistic analysis of the Andreev reflection [2]. This purely informational approach is particularly important given the narrow parameter space that separates the now rich variety of techniques to directly probe superconductivity, enabling robust control over crossovers between non-contact, near-contact, multiple Andreev reflection as well as quasiparticle tunneling in atomic-scale junctions.

Research sponsored by Division of Materials Science and Engineering, Basic Energy Sciences, Office of Science, US Department of Energy. SPM experiments were carried out as part of a user project at the Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, a US Department of Energy Office of Science User Facility.

1. W. Ko, J. Lado, P. Maksymovych, Nano Lett. 22, 4042 (2022).

2. W. Ko, E. Dumitrescu, P. Maksymovych, Phys. Rev. Res. 3, 033248 (2021).

Actinides and Rare Earths Focus Topic
Room 318 - Session AC+LS+MI-WeA

Chemistry and Physics of the Actinides/Rare Earths

Moderator: Krzysztof Gofryk, Idaho National Laboratory

2:20pm **AC+LS+MI-WeA-1** ***Novel Preorganized Ligands for Selective and Efficient Separation of f-Elements , Santa Jansone-Popova,*** Oak Ridge National Laboratory **INVITED**

Selective separation of f-elements (lanthanides and actinides) is challenging to realize due to their very similar properties. For example, lanthanides exist predominantly in 3+ oxidation state and their ionic radii decrease across the lanthanide series on average by only 0.01 Angstrom per unit increase in atomic number. Organic molecules (ligands) capable of magnifying these effects and selectively recognizing one element over another are extensively sought after. Implementation of such ligands in separating f-elements would result in substantial cost and energy savings. The neutral organic molecules decorated with at least four donor atoms (oxygens and/or nitrogens), designed to complex with metal ions and that do not undergo conformational change in the process, demonstrate exceptional size selectivity.[1-3] The innate rigidity and size of the cavity in addition to the electronic structure of ligands provide the means to control the selectivity across the trivalent f-element series by design. On the contrary, organic molecules with donor groups that are connected to freely rotating single bonds show high affinity for metal ions that are more Lewis acidic.[4] Superior performance of preorganized ligands in two immiscible solvent system in selectively separating adjacent lanthanides or lanthanides from actinides will be discussed in detail. More specifically, the chemistry of hydrophobic and hydrophilic bis-lactam-1,10-phenanthroline-based ligands having four donor atoms will be presented, focusing on the separation of adjacent lanthanides (e.g., Nd-Pr, Tb-Gd, Ho-Dy) and

Americium-Europium pair separation. Additionally, the contrasting performance of rigid ligands decorated with two to four donor atoms will be shown and compared to their non-preorganized counterparts.

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[2] Karslyan, Y.; Sloop, F. V.; Delmau, L. H.; Moyer, B. A.; Popovs, I.; Paulenova, A.; Jansone-Popova, S. *RSC Adv.*, **2019**, *9*, 26537.

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3:00pm **AC+LS+MI-WeA-3 Impact of Noncovalent Interactions on Actinide Structural Chemistry***, **Karah E. Knope,*** Georgetown University*; J. Wacker,* Lawrence Berkeley National Lab*; M. Shore,* Georgetown University **INVITED**

Noncovalent interactions (NCIs) have received significant attention over the past several years. This interest is fueled by recent examples that have shown that these interactions, which exist beyond the first coordination sphere of a metal ion, can be used to isolate novel structural units, push chemical equilibria, and tune redox behavior. As illustrated by these examples, it has become clear that consideration of NCIs is important for understanding the overall chemical behavior of a metal ion. Taken together with our group's interest in the factors that govern actinide speciation and reactivity, our recent work has thus focused on the solution and solid-state structural chemistry of actinide complexes and clusters that form from acidic aqueous solution in the presence of heterocycles capable of N-H hydrogen bonding interactions. Specifically, we have examined the identity (i.e. composition, charge, coordination number) of actinide structural units that precipitate from monoanionic ligands systems including Br^{1-}, Cl^{1-}, and NO_3^{1-} with N-heterocycles ranging from pyridinium to terpyridinium. While bromide, chloride, and nitrate all form weak relatively weak complexes with the actinides (Th-Pu), clear effects of NCIs are present only in the chloride ligand system with chloride rich (e.g. $[Th(H_2O)_2Cl_6]^{2-}$) to chloride poor (e.g. $[Th(H_2O)_7Cl_2]^{2+}$) complexes having been observed. By contrast, speciation is much more limited in the Br^{1-} and NO_3^{1-} ligand systems. Presented here will be an overview of our experimental and computational efforts to understand the effects of NCIs on phase formation.

4:20pm **AC+LS+MI-WeA-7 XPS Characterization of a Pu-7at.%-Ga Alloy***, **Paul Roussel,*** AWE, UK*; K. Graham, S. Hernandez, J. Joyce, T. Venhaus,* Los Alamos National Laboratory

Gallium is often used in small concentrations (<10 at. %) as an alloying element with plutonium to stabilize the face centred cubic phase.Most XPS analyses of these plutonium materials have focused on low concentration alloys (< 4 at. %) where it is difficult to measure the signal and effects of gallium.Here we report the analysis of a higher alloy concentration of $Pu_{0.93}Ga_{0.07}$ in the as received state, during sputter depth profiling and following oxidation either from the addition of Langmuir quantities of oxygen or the in situ environment of the ultra high vacuum system.Quantification of the spectra has been undertaken by comparison of the elastic peak intensity and this has allowed us to test the recently reported relative sensitivity factors for plutonium [1]. The higher alloying concentration has permitted quantification of gallium in both the metal and oxides and, for the first time, the gallium chemical state plot for both alloy and oxide has been determined along with those of plutonium and oxygen.In addition to this we highlight a novel method to quantify the C1s peak which overlaps with the $Pu5p_{1/2}$ photoemission line and demonstrate the effect of gallium on the in situ oxidation rate of this alloy.

1) P. Roussel, A. J. Nelson, Quantitative XPS of plutonium: Evaluation of the Pu4f peak shape, Relative Sensitivity Factors and estimated detection limits, Surf. Interface Anal. https://doi.org/10.1002/sia.7083.

4:40pm **AC+LS+MI-WeA-8 Nanoscale Uranium Oxide: Correlating Colloidal Synthesis Pathways with Structure at the Atomic and Nanometer Length Scale***, **Liane Moreau,*** Washington State University

Nanoscale uranium oxide is of interest for the development of advanced nuclear fuels and its importance in the corrosion of conventional fuel pellets and trends in uranium mobility within environmental systems. Knowledge of nanoscale properties of uranium oxide, however, are limited due to 1) a lack of synthetic methods capable of forming monodisperse actinide oxide nanoparticles and 2) the challenges associated with characterization of complex interfaces. Organic-phase colloidal approaches prove promising towards the synthesis of actinide oxide nanoparticles due to precedence for formation of highly monodisperse transition metal oxide nanoparticles, and the capability to synthesize particles in rigorously air- and water-free environments. Three systems will be discussed which exploit colloidal uranium oxide synthesis. The first explores oxidation kinetics in UO_2 nanoparticles. Synthesis is paired with X-ray diffraction and X-ray spectroscopy to compare nanoparticle oxidation trends with those observed in bulk counterparts under controlled oxidative environments. The second traces the formation mechanism of UO_2 nanoflowers and demonstrates the role of solvent interactions in anisotropic growth. The established growth patterns are particularly interesting as anisotropic growth in transition metal counterparts have traditionally depended on surface binding species and trace impurities rather than solvent chemistry. The third system investigates the deposition of uranium oxide onto iron nanoparticle cores, which serves as an analogue to environmental systems where uranium and plutonium have shown to preferentially bind to Fe-based minerals. The high-surface area particles provide a means to investigate the interface in atomistic detail. In describing the aforementioned systems, X-ray focused approaches and characterization method development will be discussed, which prove critical to resolving structural attributes and making connections between synthetic parameters and resulting atomic and nanoscale structure.

5:00pm **AC+LS+MI-WeA-9 Chemical Speciation Mapping of Spent Nuclear Fuel Using Soft X-Ray Spectromicroscopy at the Advanced Light Source***, **Alexander Ditter**, D. Smiles, D. Lussier,* Lawrence Berkeley National Laboratory (LBNL)*; A. Altman,* Northwestern University*; M. Bachhav, L. He,* Idaho National Laboratory*; M. Mara,* Northwestern University*; S. Minasian,* Lawrence Berkeley National Laboratory (LBNL)*; C. Degueldre,* Lancaster, UK*; D. Shuh,* Lawrence Berkeley National Laboratory (LBNL)

A nuclear reactor is a complex environment, with high temperatures, large temperature gradients and a multitude of fission products in various states. Spent nuclear fuel offers a key window into this environment, but is an important object of study in its own right, particularly with regards to the release of radioisotopes into the environment. The oxidation of spent nuclear fuel is especially important as this can govern the transport and solubility of fission products. To study this process, a focused ion beam (FIB) was used to make thin sections of a low burnup spent fuel pellet at Idaho National Laboratory. These FIB sections were then measured at the O K-edge, U $N_{4,5}$-edges and Ce $M_{4,5}$-edges at the scanning transmission x-ray microscope (STXM) at Advanced Light Source (ALS) Beamline 11.0.2. O K-edge results were analyzed by a modified form of non-negative matrix factorization and revealed two main components, the bulk of the sample which is made up primarily of UO_2, and a thin (est. 8 nm) layer of UO_{2+x} on the surface of the FIB section. This oxidation occurred after FIB sectioning as a thin layer over the entire sample. Cerium measurements showed that the Ce (~ 0.4 wt. %) is at least predominantly in the 3+ oxidation state, though a small contribution of tetravalent cerium cannot be ruled out, representing the first known measurements of Ce oxidation state in spent nuclear fuel. This work lays the foundations for future STXM measurements of FIB sections of spent nuclear fuel which can be expanded to mixed-oxide, uranium nitride, or other advanced fuels.

5:20pm **AC+LS+MI-WeA-10 Structural, Thermodynamics, and the Electronic Properties of Al, Ga, In, and Tl Stabilized δ-Pu***, **Sajib Barman**, S. Hernandez,* Los Alamos National Laboratory

The 5*f* electrons in plutonium show mystifying character contrary to other elements in the periodic table, where there are six solid state phases of plutonium that undergo five solid-state phase transformations in a relatively short temperature range. The low temperature α-phase is brittle and has a monoclinic structure where the high temperature δ-phase is ductile and has an FCC structure. From a metallurgical point of view, the ductile δ-Pu is mostly important due to its favorable elasticity compared to the brittle α-Pu. Therefore, stabilizing δ-Pu at room temperature can be done by alloying with Group IIIA elements (X = Al, Ga, In, and Tl). Nevertheless, the alloyed δ-Pu stability zones highly depend on the alloying content, where the stability zone decreases with increasing atomic number of the Group IIIA elements. In this work, we will present a systematic density functional theory investigation of the thermodynamic stability of alloyed δ-Pu with Group IIIA elements as a function of alloying content (3.125, 6.25, and 9.375 at. %). We have calculated that the δ-Pu-Ga alloys have the highest thermodynamic stability compared to the other Group IIIA alloys, where the stability trend follows Pu-Ga > Pu-Al > Pu-In > Pu-Tl at 0K. After volume optimization, the volume contracts for Pu-Ga and Pu-Al alloys, while the volume expands for Pu-In and Pu-Tl alloys with increasing alloy content. Finally, we will show the electronic structure analysis to discuss the electronic interaction between Pu and the Group IIIA elements within the δ-matrix.

This work was carried out under Los Alamos National Laboratory's LDRD-DR project #20210001DR.

Applied Surface Science Division
Room 320 - Session AS+CA+HC+LS-WeA

Shining a Light on Surface Chemical Metrology: In Memory of Martin Seah

Moderators: Donald Baer, Pacific Northwest National Laboratory, **Alexander Shard**, National Physical Laboratory, UK

2:20pm **AS+CA+HC+LS-WeA-1 Metrology Lights the Way for Advances in Metabolic Imaging at the Single-cell Scale**, ***Ian Gilmore,*** National Physical Laboratory, UK **INVITED**

The international community recently paid homage to Martin Seah in a Special Issue of Surface Interface Analysis [1] with reminiscences, biographical accounts of his considerable achievements, reviews and research articles. The collection takes its title “Shining a light on surface chemical analysis” from Martin’s research career of over 5 decades dedicated to guiding the community to make better measurements in traditional and emerging areas of surface chemical analysis. Where there was darkness, he brought light. Here, we begin with a retrospective look at Martin’s considerable achievements in XPS, AES, SIMS, AFM and leadership in International Standardisation.

Martin was never one for too much retrospection though and was always full of energy and enthusiasm to tackle the issues of tomorrow. We therefore show how by using Martin’s methodology that metrology is lighting the way for metabolic imaging at the single-cell scale, which is of critical importance in the development of new pharmaceuticals, understanding tumour heterogeneity and fundamental biological studies to understand metabolic rewiring in diseases.

References

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3:00pm **AS+CA+HC+LS-WeA-3 Two-Point Calibration Method for Quantifying Organic Binary Mixtures Using SIMS in the Presence of Matrix Effects**, ***Alexander Shard,*** National Physical Laboratory, U.K.*; A. Miisho,* Kobelco, Japan*; J. Vorng, R. Havelund, I. Gilmore,* National Physical Laboratory, U.K.*; S. Aoyagi,* Seikei University, Japan

Quantification of composition for organic mixtures is required in the analyses of technological materials from organic electronics to drug delivery systems. The molecular specificity of secondary ion mass spectrometry provides an unparalleled ability to distinguish organic materials, however it is difficult to use for quantitative analysis. In a few cases, there is a linear dependence between the composition, expressed as a ratio of component volumes, and the secondary ion intensities, expressed as a ratio of intensities of ions from each component. However, this ideal relationship fails in the presence of matrix effects and linearity is observed only over small compositional ranges, particularly in the dilute limits. We present an empirical method which introduces a power law dependence between the intensity ratio and the volume fraction ratio. A physical model of the organic matrix effect is employed to test the limits of the method and a mixed system of 3,3’-bis(9-carbazolyl) biphenyl and tris(2-phenylpyridinato)iridium(III) is used to demonstrate the method. In practice, we describe a two-point calibration, which determines both the exponent in the power law and the sensitivity factor for the conversion of ion intensity ratio into volume fraction ratio. We demonstrate that the two-point method significantly improves the accuracy of quantification compared to a one-point, linear calibration and is valid over a wide compositional range. Since the method enables the use of clearly identifiable secondary ions for quantitative purposes and mitigates commonly observed matrix effects in organic materials, the two-point calibration method could be of significant benefit to SIMS analysts.

3:20pm **AS+CA+HC+LS-WeA-4 OrbiSIMS Metrology: Optimization of Inorganic Depth Profiling using Ge and Sb Delta-layer Samples***, Y. Zhou,* National Physical Laboratory, UK*; A. Franquet, V. Spampinato,* IMEC, Belgium*; A. Pirkl,* IONTOF GmbH, Germany*; W. Vandervorst, P. Van Der Heide,* IMEC, Belgium*;* ***Ian Gilmore,*** National Physical Laboratory, UK

In 2017, NPL introduced the 3D OrbiSIMS instrument [1] for sub-cellular resolution molecular imaging with high-mass resolution and mass accuracy (> 240,000 at m/z 200 and < 2 ppm, respectively). Since then, IONTOF installed multiple Hybrid SIMS systems around the world with a growing range of applications, largely in, but not limited to, the life-sciences.[2,3] The dual ToF-MS and Orbitrap-MS analyzers combined with Bi liquid metal, gas cluster, and low energy $O_2^+$and Cs^+ ion beams provide a highly versatile platform for materials science studies.

Since the Orbitrap-MS is designed to operate with a continuous ion source, the instrument is well configured to take advantage of single ion beam depth profiling approaches. For example, Sul et al[4] recently demonstrated the ability to sputter depth profile a blue phosphorescent OLED device using GCIB sputtering with Orbitrap-MS. Similarly, Spampinato used the high-mass resolving power of the Orbitrap-MS to study thin EUV photoresist films where ToF-SIMS suffered from severe molecular interferences. [5] Moreover, there is growing interest in the application of the OrbiSIMS to inorganic semiconductors. Franquet et al[6] recently showed how the high mass resolution of the Orbitrap-MS analyzer combined with 2 keV Cs^+ sputtering enabled the composition of SiGe architectures down to < 20 nm to be determined with improved accuracy using the Self Focusing SIMS methodology.[6]

In this study, we use a sample consisting of 8 Ge delta-layers with a spacing of 4.8 nm in a silicon matrix. The thickness of each delta-layer is ~0.2 nm with a concentration of below 1 atom%. A second sample consisting of 5 Sb delta-layers with a spacing of 10 nm in a silicon matrix was also used. A sputter gun using either O_2^+or Cs^+ between 1 keV and 2 keV was used for both sputtering and analysis with Orbitrap-MS detection. The optimization of instrument parameters including sputter rate, injection time and sputter beam energy on the depth resolution (λ_g, λ_d and Gaussian broadening)[7]will be discussed.

1. M.K. Passarelli, et al, I.S. Gilmore, Nat. Methods, 14(2017)12, 1175-1183.

2. C.L. Newell, et al, A.P. Gould, Angew. Chem, 59(2020)41, 18194-18200.

3. J. Zhang, et al, I.S. Gilmore, P.D. Rakowska, Anal. Chem., 92(2020)13, 9008-9015.

4. S. Sul, G. Trindade, J. Kim, et al, https://www.researchsquare.com/article/rs-1279729/v1 (2022).

5. V. Spampinato, et al, P. V.D. Heide, Anal.Chem. 94 (2022)5, 2408-2415.

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7. M.G. Dowsett, et al, P.N. Allen, J. Vac. Sci. Technol. B 12 (1994)186.

4:20pm **AS+CA+HC+LS-WeA-7 Complementary Perspectives on the Impacts of Martin Seah on Surface Analysis**, ***Don Baer,*** Pacific Northwest National Laboratory **INVITED**

Throughout his more than four decade career Dr. Martin Seah had a major impact on quantitative surface analysis and the surface analysis community. There were many facets to his activities, interactions, and leadership and most of those who interacted with him knew only a portion of his many contributions. This talk will describe ways that he impacted my career and some of the activities that may have been less visible to many in the surface analysis community. Accurate quantitative surface analysis was a theme throughout his career. My introduction to his work was associated with measurements of the segregation of trace elements to the grain boundaries of metals and metal alloys.In the 1970s understanding of the challenges to quantitative analysis of electron spectroscopy was evolving and results were often inconsistent and sometimes a source controversy. Work by Seah and Hondros was important to put these measurements on a sound foundation. An important trait of Martin’s work was his ability to identify needs or information gaps and to proceed to fill them.There are many examples of this, including application of XPS to measure very thin oxide films on silicon wafers, simple models of electron mean free path lengths, models for understanding sputtering rates of cluster ion sources and the development of consistent terminology for surface methods and analysis. Martin made significant and enjoyable efforts to communicate information to the community and offered encouragement to other researchers in a variety of ways.Although his presentations seemed to be spontaneous and often full of humor, they were always well thought out and delivered clear and important messages. In viewing one of my presentations the year of his death, he made many complementary remarks in email correspondence, but chided me for having too much information on my closing slide.He said that it was important to have a simple clear final message for each talk. A portion of his influence and success was due to many delightful professional and informal social interactions.When he liked a presentation, he would offer a simple "well done" and I very much valued such comments when I received them.At an American Chemical Society Meeting in New York City we went to the half price theatre ticket booth and chose to attend not a Broadway musical but a delightful Arthur Miller play with almost no audience.

5:00pm **AS+CA+HC+LS-WeA-9 The 'Crypto-Electron' Question: XPS of Tribo-electrified Insulators***, Hagai Cohen,* Perlman bdg., The Weizmann Institute, Israel

Recent experiments on tribo-electrification have raised fundamental questions on the role of electrostatic charge in chemical and physical surface activity. Cryptolectrons were claimed to be created and, subsequently, be exploited to establish 'single-electrode electrochemistry'. However, our XPS study of this problem reveals methodological issues that were not taken into account. I will show that XPS proposes an interesting template for studies of various processes under controlled surface charge conditions, with which limiting factors on the magnitude of electrostatic surface fields can be extracted. How would a cryptoelectron, if existing, look like and can XPS imitate this creature to some extent – these questions and related ones will be discussed.

5:20pm **AS+CA+HC+LS-WeA-10 Effects, in XPS, on Composition Determination Using Different Background Removal Procedures: Single Crystal Fe_2O_3 as an Example***, Christopher R. Brundle,* C R Brundle and Associates*; B. Crist,* xpsdata*; P. Bagus,* University of North Texas

Precision achievable in XPS is very good. Accurate quantitation from relative peak intensities is more difficult, even for homogenous materials. Normalizations for σ and λ are required, but the procedures are by now well understood. The accuracy of removing a background to establish the intrinsic spectrum is on less secure ground. There are several approaches, and implementation requires adjustment of parameters either manually, or automatically by the software used. The situation is at its most unsure when an XPS core level "peak" consists of overlapping structure spread over a wide (up to several 10's ev) BE range, such as with Fe 2p (multiplet splitting; shake structure) and O1s (shake) in Fe_2O_3 (1). The situation is similar for many other transition metal compounds. We examine, for a hematite single crystal, Tougaard and Shirley based background removals. Our conclusion is that the high BE endpoint, ie. where the person taking, or analyzing, the data sets the background to meet the experimental spectrum (implying there is no further intrinsic signal beyond that BE) is critical for high composition accuracy. Obviously, theory input on where intrinsic substructure ends helps to establish what is a reasonable endpoint (1). It is quite possible to adjust endpoints (Fe2p and O1s) to return the "expected" answer, 40% atomic Fe, but this is arbitrary, and, of course, assumes 100% accuracy of the relative σ and relative λ in addition to assuming a) that the Transmission Function, TF, of the instrument has been accurately calibrated, and b) that a small signal from surface OH is properly accounted for. So, in this presentation we are more concerned with the *range in composition* returned by each method (and variations within each method), rather than absolute values, when different, but plausible, endpoints are used. We also find that results differ using high energy resolution and low resolution. The two effects together amount to a ~4% variation in determined Fe %age for Tougaard and ~6% for Shirley. We stress that this work represents a practical approach, using the particular versions of the Tougaard and Shirley software available with the instrument involved, and no sample treatment within the instrument, which we believe is the way most practical XPS analyses are actually performed. Finally, we discuss the reasons for the differences observed and examine other possible procedures.

1) Origin of the complex main and satellite features in Fe 2p XPS of Fe_2O_3, Paul S. Bagus, Connie J. Nelin, C. R. Brundle, B. Vincent Crist, N. Lahiri, and Kevin M. Rosso, PCCP 2022 and references therein.

5:40pm **AS+CA+HC+LS-WeA-11 XPSOasis.org: the XPS Peak-Fitting Network***, Alberto Herrera-Gomez,* CINVESTAV, Mexico*; D. Herrera-Rendon, E. Aguilar-Diaz,* RDATAA, Mexico

The XPSOasis Web platform aims to make available to the XPS community, free of charge, tools that facilitate communication between XPS users; this includes discussion forums, peak-fitting databases (one for each core-level), dynamic communication between users, and free data analysis software. The web platform allows users of different fitting software to easily upload posts to ask questions with images of the fitting that concern them. To answer the questions, the posts contain the data, allowing knowledgeable users to download and work on the recommendations.Novice users can consult expert users in direct conversations. Technical discussions on the analysis of XPS data can also be held.

To hook expert (and non-expert) users, the participation is rewarded with *Spicer* points, which are accumulated through *likes* in their posts (given by other users) and when one of their posts reaches the peak-fitting data base (which is a decision of the corresponding moderator).Categories are defined in terms of the points.User belonging to certain categories can compete to become moderators of a certain core-level forum and database.They could also offer courses.Another advantage of having posts in the database is that they become the norm and could be cited.

The usefulness of XPSOasis.org is a function on the availability of peak-fitting parameters for each core-level for each element under a variety of chemical environments.Since it is a user-based platform, it becomes more useful as the number of users posts increases.This is a possible solution (which will, in fact, be provided by the XPS community itself) for the erroneous XPS analyses all too common in the scientific literature.

6:00pm **AS+CA+HC+LS-WeA-12 ASSD Peter Sherwood Mid-Career Award Talk: Advancing X-ray Photoelectron Spectroscopy (XPS) Methodologies for Materials Research***, Mark Biesinger*[1], Surface Science Western, Canada **INVITED**

Chemical state X-ray photoelectron spectroscopic (XPS) analysis of first row transition metals and their oxides and hydroxides is challenging due to the complexity of the 2p spectra resulting from peak asymmetries, complex multiplet splitting, shake-up and plasmon loss structure, and uncertain, overlapping binding energies. Our work has shown that all the values of the spectral fitting parameters for each specific species, i.e. binding energy (eV), full width at half maximum (FWHM) value (eV) for each pass energy, spin-orbit splitting values and asymmetric peak shape fitting parameters, are not all normally provided in the literature and databases, and are necessary for reproducible, quantitative chemical state analysis.

We have worked toward a consistent, practical, and effective approach to curve fitting based on a combination of 1) standard spectra from quality reference samples, 2) a survey of appropriate literature databases and/or a compilation of literature references, 3) specific literature references where fitting procedures are available and 4) theoretical fittings, where available, of multiplet split reference spectra. The use of well characterized standard samples and fitting of the entire peak shape has been shown to increase our ability to accurately identify and (semi) quantify the various species present in mixed oxide/hydroxide systems [1,2,3]. Additional chemical information has also been elucidated from Auger parameters and by using Wagner plots [4,5]. The unique spectral shapes of the LMM Auger peaks for these transition metals, particularly for Cu [5], have also been shown to be of use for chemical speciation. These methods have been shown to be effective in a wide variety of applications.

An overview of these curve-fitting methodologies will be presented along with examples highlighting how these methods have been used to elucidate complex sample chemistries.A recent assessment of available charge corrections procedures for insulating samples will also be shown [6].

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1. M.C. Biesinger, et al., *Surf. Interface Anal.***41** (2009) 324.

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[1] **ASSD Peter Sherwood Award**

Electronic Materials and Photonics Division
Room 330 - Session EM-WeA

Compound Semiconductors
Moderator: Erica Douglas, Sandia National Laboratories

5:20pm **EM-WeA-10 Strain-Induced Semiconducting to Metallic Phase Transition in Suspended Mote$_2$ using a Single-Ion Conductor***, **Shubham Awate**,* University of Pittsburgh*; J. Xu,* Rochester Institute of Technology*; J. Liang, B. Mostek,* University of Pittsburgh*; B. Katz,* Pennsylvania State University*; R. Muzzio,* Carnegie Mellon University*; V. Crespi,* Pennsylvania State University*; J. Katoch,* Carnegie Mellon University*; E. Backman, S. Fullerton-Shirey,* University of Pittsburgh

Commonly studied transition metal dichalcogenide (TMD) crystals exhibit polymorphism, where the electronic structure of the material changes significantly with a change in the crystal structure. $MoTe_2$ has gained particular interest because the potential energy difference between the semiconducting 2H and semi-metallic 1T' phase is the lowest (40 meV) among TMD polymorphs, making it promising for low voltage phase change memory and transistors. Although the 2H phase is the most stable form, it can be transformed to 1T' by 0.3 - 3% by tensile strain thereby causing a large change in the electronic conductivity. Recent studies have experimentally shown this phase transition by mechanically stretching the entire substrate or applying local mechanical strain using atomic force microscopy (AFM) tip, but both strain methods would be difficult to implement in CMOS. What is needed is a straining mechanism driven by field-effect, where a single device can be controlled electrically by a nearby gate.

Here, we employ an 'ionomer' or single-ion conductor to impart strain. An ionomer contains mobile cations but has anions that are covalently bonded to a polymer backbone. Under an applied electric field, the cations accumulate at the $MoTe_2$ surface, effectively controlling electron transport in the material, while anions maintain their position in the polymer backbone creating a charge imbalance. The imbalance causes the ionomer to bend, which then induces strain in the $MoTe_2$.

In this work, the electrical and structural properties of a suspended $MoTe_2$ FET are measured simultaneously using a home-built set-up combining electrical measurements with Raman spectroscopy. With no gate voltage (V_G) applied, the insulating 2H phase is confirmed. For $V_G > 2.5$ V, the 1T' phase is detected by a significant decrease in the electrical resistance accompanied by a characteristic 1T' peak in the Raman spectra. Mapping the 2H and 1T' peaks across the entire flake reveals that the phase transition is reversible (i.e., the flake reverts to the semiconducting 2H phase when the voltage is removed), which is an essential feature of memory. The output characteristic of the FET shows a large change in the I_D-V_G slope for $V_G > 1.5$ V. Further, metallic conduction is confirmed by the positive temperature coefficient of resistance for $V_G = +2$ and $+3$ V. Lastly, time-dependent Raman spectroscopy is performed to study the phase change dynamics. The demonstrated gate-controlled reversible straining method can be easily extended to strain other types of two-dimensional materials to explore fundamental properties as well as discover new device mechanisms.

5:40pm **EM-WeA-11 Investigation of Thermal Stability of Pure-Metal Schottky Contacts to β-Ga_2O_3***, **Elizabeth Favela**, K. Zhang, A. Ho, S. Kim,* Carnegie Mellon University*; K. Das,* North Carolina State University*; L. Porter ,* Carnegie Mellon University

Due to its ultra-wide band gap ($E_G \sim 4.8$ eV) and the availability of melt-grown single-crystal substrates, gallium oxide (Ga_2O_3) has attracted intense interest for (opto)electronic devices that can operate under extreme conditions. However, for these devices to operate reliably, electrical contacts to Ga_2O_3 that are chemically and electrically stable at elevated temperatures must be demonstrated. In this study we investigated the electrical properties, interfacial chemistry and surface morphology of Co/Au and Ni/Au Schottky contacts on Sn-doped ($N_D = 10^{18}$ cm^{-3}) (-201) β-Ga_2O_3 substrates through two different annealing series. Current-voltage and capacitance-voltage measurements were conducted at room temperature after sequential annealing treatments totaling >400 h at 300 °C and >150 h at 500 °C in air. Schottky barrier heights were relatively stable through the annealing series at 300 °C. However, gradual degradation in the electrical behavior was observed through the annealing series at 500 °C. Whereas the contacts were relatively stable after 300 °C anneals, characterizations using scanning transmission electron microscopy, energy dispersive x-ray spectroscopy, and scanning electron microscopy of samples annealed at 500 °C showed substantial changes in morphology, multi-element diffusion, and phase segregation within the contacts. The results suggest that these pure-metal contacts could be useful in Ga_2O_3 Schottky diodes at temperatures below, or possibly up to, 300°C. However, alternative contact compositions, possibly incorporating metal-oxides [1], will be required for Ga_2O_3-based device operation at or above the 300 °C temperature range. The results of this work in context of other Ga_2O_3 contact studies and the implications for future research directions will also be presented.

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6:00pm **EM-WeA-12 Electrical and Chemical Effects of Metal Contacts to β-Ga_2O_3 Surfaces***, **Luke Lyle**,* Pennsylvania State University

Over the last decade significant progress has been demonstrated for -Ga2O3, with its ultrawide bandgap of 4.6-4.8 eV, controllable range of n-type, shallow dopants (Sn, Si, Ge), and a scalable melt-growth process allowing the production of large-area, native substrates this material has garnered strong interest for applications as UV photodetectors and high-power electronics. A critical piece of development for ultrawide bandgap materials is the optimization of the metal-semiconductor interface for high-power applications. This talk focuses on the electrical properties of various metallizations to differently oriented β-Ga2O3 crystals and focuses on the resulting chemistry of certain metal-semiconductor interfaces. The Schottky barriers of Ti/Au, Mo, Co, Ni, Pd, and Au on (100) β-Ga2O3 substrates were analyzed using a combination of current-voltage (J-V), capacitance-voltage (C-V), and current-voltage-temperature (J-VT) measurements. The ideality factors and Schottky barrier heights from J-V and C-V methods are documented and discussed. J-V-T measurements of Ti/Au, Co, and Pd diodes reveal inhomogeneity of the Schottky energy barrier. These combined results reveal a strong positive correlation between the calculated Schottky barrier heights and the metal work functions: the index of interface behavior, S, for J-V and C-V data. Additionally, Ti and Au metallizations reveal peculiar electrical properties (higher ideality factors, different J-V and C-V Schottky barrier heights, etc) and further characterizations are pursued. Au contacts to (100) β-Ga2O3 were subsequently examined with transmission electron microscopy (TEM) due to the electrical properties exhibited via J-V and C-V measurements. The contacts exhibited a chemical reaction with void formation 5-20 nm below the Au/β-Ga2O3 interface, a reacted region at the interface that is structurally dissimilar to the bulk β-Ga2O3 structure, the presence of Ga interstitials diffusing to the metalsemiconductor interface, and EDS mapping reveals Ga diffusion into the Au overlayer. Chemical measurements of Ti/(010) and Ti/(001) β-Ga2O3 contacts were examined with x-ray photoelectron spectroscopy (XPS). XPS revealed partial Ti oxidation at both interfaces in the as-deposited condition, with more Ti oxidation on the (001) β-Ga2O3 epilayer surface than the (010) β-Ga2O3 substrate surface. The amount of oxidized Ti increased with annealing temperature. J-V and C-V measurements of contacts made from these devices reveal a strong orientation dependence of the electrical properties of Ti/β- Ga2O3 diodes.

Fundamental Discoveries in Heterogeneous Catalysis Focus Topic
Room 321 - Session HC+AS+SS-WeA

Bridging Gaps II: Single Atom Alloys and Desirable Defects
Moderators: Rachel Farber, University of Chicago, **Gareth Parkinson**, TU Wien, Austria

3:00pm **HC+AS+SS-WeA-3 Atomic-Scale Structure-Function Relationships of Pt-based Copper Oxide Single-Atom Catalysts***, **Audrey Dannar**, A. Schilling, G. Giannakakis, A. Therrien, E. Sykes,* Tufts University

Single-atom catalysts comprised of isolated metal atoms anchored on oxide supports have recently gained considerable attention for their potential to improve the activity and or selectivity of important industrial reactions. We have previously shown that single Pt atoms on a copper oxide thin-film are able to perform low-temperature CO oxidation without sintering, a common deactivation mechanism of single-atom catalysts. Using a combination of scanning tunneling microscopy, infrared and x-ray photoelectron spectroscopy, and temperature programmed desorption we elucidated the atomic-scale surface structure of these model catalysts and related that structure to catalytic function. We found that Pt atoms have a preferred binding site on the oxide surface and that they can oxidize CO, but not H_2. These fundamental surface results were leveraged in the design of nanoparticle analogs that were active and selective for the preferential oxidation of CO. In order to extend this approach to bulk oxides we have begun characterizing the 111 facet of a Cu_2O single-crystal which better mimics the Cu_2O particles present in high surface area catalysts. Scanning tunneling microscopy images of the $Cu_2O(111)$ surface reveal atomic-scale structures that may be responsible for the reactivity observed in real catalysts. Low-energy electron diffraction patterns reveal reconstructions in the model catalyst surface induced by exposure to reducing or oxidizing conditions, which is important in terms of how the active sites, and their coordination to the oxide support evolve under relevant reaction conditions. Taken together, our thin-film and bulk copper oxide surfaces decorated with isolated Pt atoms provide useful model systems with which to parse out atomic-scale structure-function relationships that inform the rational design of novel catalysts.

4:20pm **HC+AS+SS-WeA-7 Comparison Study of Several Transition Metals on Two Different TiO_2 Model Supports: Anatase TiO_2 (101) and Rutile TiO_2 (110)***, **Lena Puntscher**, K. Daninger, P. Sombut,* TU Wien, Austria*; M. Meier,* University of Vienna, Austria*; M. Schmid,* TU Wien, Austria*; C. Franchini,* Alma Mater Studiorum, Università di Bologna, Bologna, Italy*; U. Diebold, G. Parkinson,* TU Wien, Austria

Single-atom catalysis (SAC) offers an opportunity to minimize the amount of precious catalyst material required for traditional heterogeneous catalysis and to "heterogenize" reactions presently requiring homogeneous catalysis; this would eliminate the problem of separating catalyst and product, while retaining the excellent selectivity and activity of homogeneous catalysts [1].

Unravelling how metal atoms bind to oxide supports is crucial for a better understanding of the SAC´s catalytic properties. Using STM and XPS, we compare the adsorption geometry and stability of several transition metals on TiO_2 model supports: anatase $TiO_2(101)$ and rutile $TiO_2(110)$ [2] and the influence of water on the dispersion of these systems.

This study points out the importance of metal-support interaction and the surprisingly different behaviour of the transition metals Pt, Rh, Ir and Ni on TiO_2 model supports.

42. Parkinson, G.S., *Single-atom catalysis: how structure influences catalytic performance.* Catalysis Letters, 2019. **149**(5): p. 1137-1146.
43. Sombut, P., et al., *Role of Polarons in Single-Atom Catalysts: Case Study of Me_1 [Au_1, Pt_1, and Rh_1] on TiO_2 (110).* arXiv preprint arXiv:2204.06991, 2022.

4:40pm **HC+AS+SS-WeA-8 Boron Effect Improves Catalytic Performance on Supported Pt/SiO_2 Catalysts for Dry Reforming of Methane at Reduced Temperatures***, **Carly Byron**,* University of Delaware*; M. Ferrandon, A. Kropf,* Argonne National Laboratory*; S. Bai,* University of Delaware*; M. Delferro,* Argonne National Laboratory*; A. Teplyakov,* University of Delaware

Metal nanoparticles supported on metal oxides are studied as catalysts for a variety of applications, most notably catalytic hydrocarbon reforming reactions. Platinum has shown to be a highly active catalyst for the dry reforming of methane (DRM), which converts CO_2 and CH_4 into "synthesis gas", which can be further processed to produce biofuel. However, the DRM process requires further optimization before large scale use. Our prior studies have shown that boron has a positive effect on platinum/silica catalyst for butane dehydrogenation, due to the reduction in carbon contaminant (coke) on the surface and migration of carbon deposit away from platinum active sites. Based on these findings, $Pt/B/SiO_2$ catalysts were prepared for DRM catalysis and compared with Pt/SiO_2 catalysts without boron promotion. Both catalysts had similar concentrations of platinum, but the catalytic activity after 14 hours for boron-containing catalyst was drastically improved, resulting in nearly 100% CO_2 conversion compared to 12% without boron. The reacted catalysts were investigated with synchrotron x-ray adsorption spectroscopy (XAS), transmission electron microscopy (TEM), x-ray electron spectroscopy (XPS), and Raman spectroscopy to identify the deactivating factor. It was determined that neither sintering nor coking was a significant factor in Pt/SiO_2 catalyst deactivation, instead that platinum and boron interact electronically to optimize DRM catalysis, which results in high activity at relatively low DRM operating temperatures.

5:00pm **HC+AS+SS-WeA-9 Facet Dependence of RhCu Single-Atom Alloy Structure and Reactivity***, **Yicheng Wang**, R. Hannagan,* Tufts University*; J. Schumann, M. Stamatakis,* University College London, UK*; C. Sykes,* Tufts University, UK

Direct propane dehydrogenation is a promising way to address the current propene shortage. RhCu single-atom alloys (SAAs), predicted by first-principal calculations, have recently been demonstrated to be efficient propane dehydrogenation catalysts. While RhCu model catalysts have been conducted on the (111) facet of Cu to understand the C-H activation mechanism, other facets have not been explored which is important fundamental information needed to bridge the structure gap between model catalyst and nanoparticle studies. In order to better understand the effect of the more open (100) facet, we investigated the RhCu(100) SAA surface using a combination of scanning tunneling microscopy (STM), temperature programmed desorption (TPD), reflection absorption infrared spectroscopy (RAIRS) and density functional theory (DFT). Our STM results reveal a striking difference between the alloying mechanism of Rh atoms in Cu(111) versus Cu(100) surface facets.Unlike RhCu(111) where Rh atoms tend to form dense brim in the regions above the step edges, homogeneously dispersed Rh atoms can be observed across the whole Cu(100) surface. DFT modeling indicates that the starkly different Rh distribution can be attributed to the different alloying mechanisms between the Cu(111) and Cu(100) where Rh atom place exchange into the terraces is facile on Cu(100). CO TPD and RAIRS experiments were conducted to study the Rh active sites in the RhCu(100) alloys. CO TPD experiments revealed CO desorption at both low and high temperature hinting at the existence of dicarbonyls, which had not previously been observed on SAAs. RAIRS was used to demonstrate that the low temperature peak corresponded to the transition from dicarbonyls to monocarbonyls and the high temperature peak involved the desorption of the monocarbonyls, which was further confirmed by DFT. Together, these results help us to understand the active sites in RhCu(100) SAAs and the influence of the coordination environment on the binding to Rh sites. These results will further shed light on the structural characterization of high surface area SAA catalysts.

5:20pm **HC+AS+SS-WeA-10 Crossing the Great Divide Again: Psuedo-Molecular Beams at Atmospheric Pressure***, E. High, **Christian Reece**,* Harvard University

In order to reliably predict catalytic activity, we require accurate and robust kinetic models. Fundamental surface science studies on model catalysts are generally considered the "gold standard" for measuring in-depth kinetic and mechanistic information. However, there is often a perceived difficulty in transferring this knowledge from ultra-high vacuum surface science to applied reactor conditions i.e., at elevated temperature and pressure. This misunderstanding led to the development of terms such as pressure gap. In reality this so-called pressure gap is in fact a pressure continuum, with the caveat that the catalyst state (i.e., the structure and composition) must be kept consistent across the pressure regimes [1,2]. Herein we demonstrate a high-pressure analogue to classic molecular beam experiments utilising a home-built transient flow reactor in order to directly compare results measured at UHV and at atmospheric pressure. Using CO oxidation over polycrystalline Pd as a test reaction, we find that the transient behaviour observed at UHV [3] is recreated in the transient flow reactor. Further, the fundamentally derived kinetic model that is used to describe the molecular beam experiments also recreates the transient behaviour observed at atmospheric pressure when fed into a packed bed reactor simulation.

[1] Reece, C., Redekop, E.A., Karakalos, S., Friend, C.M. and Madix, R., 2018. Crossing the great divide between single-crystal reactivity and actual catalyst selectivity with pressure transients. Nature Catalysis, 1(11), pp.852-859.

[2] Reece, C. and Madix, R.J., 2021. Moving from Fundamental Knowledge of Kinetics and Mechanisms on Surfaces to Prediction of Catalyst Performance in Reactors. ACS Catalysis, 11(5), pp.3048-3066.

[3] Libuda, J., Meusel, I., Hoffmann, J., Hartmann, J., Piccolo, L., Henry, C.R. and Freund, H.J., 2001. The CO oxidation kinetics on supported Pd model catalysts: A molecular beam/in situ time-resolved infrared reflection absorption spectroscopy study. The Journal of Chemical Physics, 114(10), pp.4669-4684.

5:40pm **HC+AS+SS-WeA-11 Self-Propagating High Temperature Synthesis of Chevrel Phase Sulfides from Elemental Precursors***, **Tessa Gilmore**, M. Pawar, P. Gouma,* The Ohio State University

Self-propagating high temperature synthesis (SHS) is a spontaneous, irreversible, combustion process that requires close to no energy to produce complex materials at high temperature through self-sustained reactions. Little is known about the mechanistic nature of this versatile process, which limits its controllability and applicability. Chevrel Phase (CP) compounds (MxMo6S8-CPs) constitute a class of multifunctional, ceramic, designer materials targeted for catalysis, battery electrodes, quantum computing, and other applications. In this research, the successful and rapid processing of the sulfide Chevrel compound Cu4Mo6S8 via SHS is demonstrated, and a mechanism is provided. Thermochemical measurements identify an atypical behavior for this SHS process where the overall reaction temperature does not surpass that of the materials with the lowest melting point. This result is attributed to intercalation assisted massive phase transformation facilitated by the use of a MoS2 precursor. Further work to synthesize the Chevrel phase using other cations is continuing.

6:00pm **HC+AS+SS-WeA-12 Growth and Activity of Ni Catalysts Supported over Ti-doped Ceria from Single Crystal Thin Films to Nanocrystals***, J. Miao, T. Ara, **Jing Zhou**,* University of Wyoming

Ceria-supported nickel catalysts have been of great interest in many important applications such as dry reforming of methane (DRM).[1] They can exhibit promising catalytic behavior owing to the unique redox properties of ceria as well as strong metal-support interactions. To enhance the thermal stability of ceria as well as improve its redox properties as a catalytic support for practical applications in catalysis, metal dopants such as Ti can be introduced into ceria. Our previous studies have shown that well-ordered (111)-oriented $Ce_{1-x}Ti_xO_{2-\delta}$ thin films can be prepared by simultaneous introduction of Ce and Ti onto Ru(0001) at 700 K in an oxygen environment.[2] The incorporation of Ti in ceria causes the partial reduction of Ce from +4 to +3 state. The films are of high quality consisting of flat terraces with surface features of ceria lattices, oxygen vacancies, Ti dopants, as well as domain boundaries. The extent of the Ce reduction and the nature of the surface structure correlate with the amount of Ti dopants in ceria. Compared to pure CeO_2(111), addition of Ti dopant in $Ce_{1-x}Ti_xO_{2-\delta}$(111) can provide unique anchoring sites and interaction for deposited Ni, which can significantly stabilize Ni as smaller particles upon heating.[3] To study as practical catalysts, powder materials of 5 wt.% Ni dispersed over a series of $Ce_{1-x}Ti_xO_{2-\delta}$ (x: 0-0.5) were prepared using sol-gel and impregnation methods and investigated for the DRM reaction with a fixed-bed flow reactor, monitored by on-line mass spectrometer and GC instruments. Incorporation of Ti into the ceria lattice forming $Ce_{1-x}Ti_xO_{2-\delta}$ was observed with Ti/Ce ratios less than 3/7 and NiO is formed over these supports. The formation of segregated titania domains was also detected in $Ce_{1-x}Ti_xO_{2-\delta}$ with higher Ti/Ce ratios ($Ce_{0.6}Ti_{0.4}O_{2-\delta}$ and $Ce_{0.5}Ti_{0.5}O_{2-\delta}$). Both NiO and $NiTiO_3$ can be formed in these Ti-rich ceria supports. Our results demonstrate that doping Ti can enhance the reducibility of ceria and tune the Ni-support interaction, which result in an enhanced coke resistance and catalytic performance of Ni in DRM. The research is sponsored by the Carbon Engineering Initiative from School of Energy Resources at the University of Wyoming.

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[2] Y. Zhou, J. Zhou, *J. Phys. Chem. Lett.***1, (11)**, 1714-1720 (2010).

[3] Y. Zhou, J. M. Perket, A. B. Crooks, J. Zhou, *J. Phys. Chem. Lett.***1, (9)**, 1447-1453 (2010).

Advanced Ion Microscopy and Ion Beam Nano-engineering Focus Topic

Room 301 - Session HI+AP-WeA

Emerging Ion Sources, Optics, & Applications

Moderators: Rosa Cordoba, University of Valencia, Spain, **Florian Vollnhals**, INAM, Germany

2:20pm **HI+AP-WeA-1 Rationalizing and Controlling the Composition and Properties of Materials Deposited Using Charged Particles***, **Howard Fairbrother**,* Johns Hopkins University **INVITED**

Focused ion beam-induced deposition (FIBID) and focused electron beam-induced deposition (FEBID) are charged particle nanofabrication techniques able to directly fabricate 2D and 3D metal-containing nanostructures from organometallic precursors. These techniques provide for precise control over beam position for nanoscale pattern writing without the use of a mask or organic solvents and as such are more environmentally benign and less wasteful than traditional lithography techniques. However, one of the biggest issues with charged particle deposition techniques is the difficulty in controlling the composition of the deposits. Indeed, the creation of pure metal nanostructures in FEBID or FIBID is often a goal for achieving optimal materials properties, but is rarely realized in practice without the need for post deposition processing. In this presentation, and using Pt as an example, I will describe how UHV surface science studies can be used to aid in the design of precursors and selection of deposition conditions that favor the creation of pure metal deposits. Examples will include, (i) the electron beam induced deposition of Pt nanostructures from $Pt(CO)_2Cl_2$, where surface science studies have identified the two sequential steps which can lead to Pt formation, notably the initial deposition event ($Pt(CO)_2Cl_{2(ads)}$ + e^-à $PtCl_{2(ads)}$ + $2CO_{(g)}$) as well as the subsequent removal of Cl via an ESD type process ($PtCl_{2(ads)}$ + e^-à $Pt_{(ads)}$ +$Cl^-_{(g)}$) and (ii) ion-beam induced deposition of Pt from $MeCpPtMe_3$ and $Pt(CO)_2X_2$ precursors, where surface science studies have revealed the greater utility of effecting deposition with lighter ions (e.g. H_2^+, He^+), due to their ability to access deposition conditions over which nearly pure Pt can be deposited as compared to heavier ions (e.g. Ar^+) where Pt sputtering rates preclude the formation of Pt. The microstructure and properties of these Pt deposits as well as the possibilities to use analogous approaches for the charged particle deposition of other metals (e.g. Au) will also be discussed.

3:00pm **HI+AP-WeA-3 Ion Beam Induced Reactions and Deposition of $Pt(CO)_2Br_2$ and $Pt(CO)_2Cl_2$***, **Mohammed Abdel-Rahman**, P. Eckhert,* Johns Hopkins University*; J. Yu, A. Chaudhary, L. McElwee-White,* University of Florida*; H. Fairbrother,* Johns Hopkins University

Direct-write lithography techniques, such as focused ion beam induced deposition (FIBID), are an attractive alternative to traditional lithographic techniques. However, traditional precursors ($Me_3PtCpMe$, $Pt(acac)_2$, for chemical vapor deposition perform poorly as FIBID precursors and result in carbon-contaminated metal deposits. To overcome this limitation, $Pt(CO)_2X_2$ (X = Br, Cl) were chosen as alternative precursors because of its low carbon content and desirable volatility for FIBID. FIBID deposits were created from commercially available $Pt(CO)_2Cl_2$ and lab synthesized $Pt(CO)_2Br_2$, complemented by *in situ* UHV studiesusing XPS and MS to determine the sequence of ion-induced processes that underly the deposition mechanism. Deposition and UHV studies were conducted with Ar^+, He^+, and H_2^+ to determine the effect of ion properties (mass and reactivity) on the deposition process. Results obtained on thin films of precursors molecules deposited on inert substrates at temperatures < 200K under UHV conditions indicate that, regardless of the ion or precursor, the deposition mechanism proceeded via rapid and complete CO loss forming PtX_2. Subsequent reactions are dominated by sputtering of the PtX_2 species with halogen loss proceeding quicker than Pt loss. Consequently, pure Pt deposits are formed beyond a critical ion dose. Although varying the ion does not alter the deposition mechanism, the relative reaction rates for the deposition and sputtering processes increase with ion size following the pattern $Ar^+ > He^+ > H_2^+$. This information can be used to select the steady-state conditions best suited to form pure Pt deposits in the absence of post-deposition purification steps.

3:20pm **HI+AP-WeA-4 Next Generation Ion Beam Resists: Sub-10 nm Helium Ion Beam Lithography***, **Scott Lewis**, G. Derose,* California Institute of Technology

A new class of metal organic resist materials that is based on a heterometallic ring (Figure 1) has been demonstrated with helium ion beam lithography while demonstrating extraordinarily high etch selectivity for silicon of >5:1 (at 8 nm half pitch (HP)) when subjected to a pseudo-

Bosch inductively coupled plasma–reactive-ion etch (ICP-RIE). The resist was designed using our latest Monte Carlo simulator (Figure 2a), which we developed because there are no simulators for ion beam lithography. Ion simulation packages such as SRIM/TRIM provide accurate data for ion penetration and propagation into a material for applications such as ion implantation, it fails to provide data on the creating a secondary electron (SE) and creating SE's cascade with further orders of SE's which are essential as they will have large effect on the sensitivity of the resist and will have a large contribution on the proximity effect. Exposing the resist to 35 keV helium ions, produced a nano pattern with a resolution of 8.5 nm HP (Figure 2b and c for a plan and tilted view), and obtained a low exposure dose of 22 pC/cm. This dose is 3 orders of magnitude lower than what is required with EBL when comparing to 100 and 30 keV electrons. To account for the low doses, this talk describes how the helium ion interacts with the resist and shows that the exposure mechanism occurs in two parts. Firstly, the helium ions are confined to the incident beam because of the resist properties of high molecular weight and low density limits the number of scattering sites that the ion encounters. Secondly, the helium ion interaction yields significantly more SE's per incident ions than electrons which had a significant contribution to the exposure efficiency. This is why that a dose lower by three orders of magnitude when compared to electron beam lithography. Through Monte Carlo simulation and X-ray photoelectron spectroscopy we will explain how the resist achieves the extraordinary high dry etch selectivity seen here (Figure 2d) where the 8.5 nm HP pattern was successfully transferred via the dry etching process into the silicon substrate. We will show through the use of Monte Carlo simulations how we were able to dramatically improve the resist by increasing its sensitivity and improving its LER while maintaining the same resolution and its high dry etch electivity. The resist has demonstrated the flexibility to be exposed by ions, electrons and EUV, which makes it a versatile lithographic material with the potential for further customization to address a wide range of nanofabrication challenges.

4:20pm **HI+AP-WeA-7 Novel Source Development for Focused Ion Beam Implantation and Irradiation***, **Edward S. Bielejec**, M. Titze, A. Katzenmeyer, A. Belianinov,* Sandia National Laboratories*; Y. Wang,* Los Alamos National Laboratory*; B. Doyle,* Sandia National Laboratories **INVITED**

We will present on Sandia National Laboratory's Ion Beam Laboratory (IBL) development of novel sources for focused ion beam implantation and irradiation capabilities.The IBL operates seven focused ion beam (FIB) systems that range in ion energy from less than 1 keV to greater than 70 MeV, including a wide range of ion species from protons (H) to lead (Pb) over a range of spot sizes from nm to mm.In particular, we will concentrate on the development of liquid metal alloy ion sources (LMAIS) for our two mass filtered FIB systems, the A&D nanoImplanter and the Raith Velion, both of which include high spatial resolution with CAD based patterning to enable the formation of arbitrary patterned implantation.

We will present an overview of the available LMAIS for the mass filters systems as well asfabrication details and results using both novel Pb and N sources.The Pb source is based on a SnPb alloy using a custom Kovar wire tip in place of the standard tungsten tip usually used for FIB applications.This source has demonstrated a long lifetime comparable to our other alloy-based sources of greater than 2000 mA*hr and less than 50 nm resolution without optimization of the tip design.The atomic N source is based on an AuSn alloy implanted with nitrogen up to the saturation limit and verified using elastic recoil detection (ERD).This N source has demonstrated a relatively short lifetime of less than 100-200 mA*hr and is limited to a total N ion production rate of approximately 2,000 to 10,000 ions/s corresponding to up toapproximately 1 fA of current of singly charged nitrogen ions.The demonstration of these sources works to continue the development of high resolution localized implantation and irradiation capabilities enabling the fabrication of custom implanted samples for cutting edge physics and quantum optics experiments.

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

5:00pm **HI+AP-WeA-9 Focused Ion Beams from GaBiLi LMAIS for Nanofabrication and Ion Imaging***, **Torsten Richter**, P. Mazarov, A. Nadzeyka, L. Bruchhaus, U. Mantz,* Raith GmbH, Germany

Focused Ion Beams (FIB) are broadly used in nanoscale science related applications, and they are inherently applied for direct nano-patterning, nanofabrication as well as for nano-analytics. FIB has become established as a direct, versatile, and precise fabrication method of smallest features at high fidelity. High demands are made on the ion beam that is used for direct FIB in terms of beam stability, patterning resolution and adjusting of the sputter yield. Liquid Metal Alloy Ion Source (LMAIS) is an emerging FIB source technology that provides a versatile solution to deliver various ion species from a single source for FIB nanofabrication to enhance resulting nanostructures [1]. However, beside nanofabrication FIB is utilized as a primary beam for SIMS analysis [2] and light ions such as Lithium in particular are well suited for sample imaging due to their low sputter yield and surface sensitive properties.

GaBiLi ion sources provide light and heavy ions from a single Liquid Metal Alloy Ion Source (LMAIS) fulfil requirements for both nanofabrication and nano-analytic [3]. Lithium, Gallium and Bismuth ions are emitted simultaneously, and ion species are separated subsequently in an ExB filter. Therefore rapid, easy, and reliable switching between light Lithium ions, and heavy Bismuth or Gallium ions enables not only novel nanofabrication processes but also satisfies analytical demands. GaBiLi allows 3D mill&image by imaging at highest lateral resolution by light Li ions and permits sample delayering at highest depth resolution with Bi ions or even Bi clusters [4]. SIMS takes advantage of optimizing either sputter yield or ionization yield of ejected ions.

In this contribution we present an overview of direct nanopatterning applications and related workflows such as 2-step bowtie nanofabrication with Lithium and Bismuth from GaBiLi (Figure 1) and ion beam imaging results that were obtained with Lithium ions (Figure 2).

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Magnetic Interfaces and Nanostructures Division
Room 330 - Session MI-WeA

Spin Landscape II (Magnetic Structures in Real and Momentum Space)

Moderator: Markus Donath, Muenster University, Germany

2:20pm **MI-WeA-1 Exploring Magnetic Reversal Behavior and Domain Structure in Perpendicular Anisotropy Layered Synthetic Antiferromagnets***, **Olav Hellwig**,* Chemnitz University of Technology and Helmholtz Zentrum Dresden-Rossendorf, Germany **INVITED**

In atomic antiferromagnets (AFMs) neither the magnetic field reversal behavior nor the magnetic domain structure are easily accessible. The reason for that is the usually very strong antiferromagnetic (AF) exchange interaction, yielding switching fields in the range of many Tesla and the even microscopically compensated magnetic moment without any significant stray fields to detect.

The situation is different in perpendicular magnetic anisotropy layered synthetic AFMs employing interlayer exchange coupled thin film multilayers with a significantly reduced AF-exchange interaction (based on the well-known Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction), which we use here to explore the magnetic reversal behavior and domain structure in layered type AFMs [1-7]. This model system also has the advantages of easy fabrication via conventional sputter deposition techniques and being compatible with smooth amorphous substrates, such as Si/SiO$_2$ wafers. Furthermore it is possible to tune the strength of the RKKY-type AF-interlayer exchange continuously via the individual thicknesses of the coupling layers (here are mostly Ru and Ir used).

The significantly reduced AF-exchange interaction strength becomes now also comparable to other magnetic energy terms, such as the anisotropy or demagnetization energy. This creates - to atomic AFMs unknown and so far unexplored - competitive magnetic energy landscapes. They lead to new reversal modes and domain structures, as we subsequently reduce the strength of the AF-interlayer exchange coupling from its dominating position [5] first below the perpendicular anisotropy energy [1-4,6,7] and second below the demagnetization energy of the layered AF system.

We will discuss the physics behind such new reversal modes and domain structures in perpendicular anisotropy layered synthetic AFMs and highlight potential applications in the arena of nanomagnetism and spintronics. Finally we will also point out in what respect such systems provide design aspects and opportunities beyond the scope of conventional atomic AFMs, in particular in the light of "Imperfectly Perfect Materials".

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3:00pm **MI-WeA-3 Influence of Underlayer Quality and Sputter Gas Pressure on Structural and Magnetic Properties of Co/Pt Multilayers***, **Rico Ehrler**, T. Uhlig, O. Hellwig,* Chemnitz University of Technology, Germany

Co/Pt multilayers (MLs) are standard systems for perpendicular anisotropy layered thin films. They are fully tunable via their layer thicknesses and number of repeats and can be easily fabricated using sputter deposition on amorphous substrates. Moreover, they were intensively investigated for their well-ordered stripe domain and bubble states [1,2] and as potential recording media [4]. Synthetic antiferromagnets with perpendicular anisotropy can also be based on these ML systems [5]. The growth conditions of the MLs are of particular importance for fine-tuning their structural and magnetic properties.

As was already shown in the literature, seed layers [4,6] and sputter gas pressure during deposition [1,3] are two very important factors that influence the structural as well as magnetic properties profoundly. The use of a specific underlayer is a common practice to define a crystalline texture for the ML on amorphous substrates. Pt and Pd are widely used as seed layer materials, sometimes in combination with additional, very thin adhesion layers to obtain a good bonding to the substrate [4,6].

For low sputter pressures, the ML is well-defined with sharp interfaces and a continuous, closed film that maintains a laterally continuous strong magnetic exchange. Under these conditions, well-ordered stripe domains and bubble states can form, which can be moved via external fields or currents laterally across the magnetic thin film [1,2]. At high deposition pressures, the MLs grow in a more isolated, granular fashion [1,3]. The layer structure shows a higher degree of disorder and a distinct reduction in the lateral exchange between adjacent grains. Such a microstructure is desirable for magnetic recording media, as it enables the static bit-wise storage of data, where every bit consists of many significantly smaller and magnetically isolated grains [1].

In this context, we will discuss the influence of the Pt seed on the structural and magnetic properties of the Co/Pt ML system, with emphasis on the impact of deposition pressure and adhesion layer. A systematic variation of the underlayer is presented for different ML deposition pressures, changing the characteristics from a continuous thin film to an isolated grain structure.

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3:20pm **MI-WeA-4 Thickness and Oxygen Growth Pressure Effects on Spontaneous Magnetization Reversal***, **Mikel Barry Holcomb**, G. Bhandari, N. Mottaghi, R. Trappen,* West Virginia University

Utilizing many techniques (bulk magnetometry, neutron reflectometry and resonant x-ray magnetic scattering), we have discovered and explored spontaneous magnetization reversal in complex oxide La0.7Sr0.3MnO3 thin films. The spontaneous magnetization reversal occurs at low applied fields and originates from the competition between different types of magnetic order. While the overall effect is observed across many sample thicknesses and oxygen growth pressures, these parameters affect the behavior systematically. Films were grown by pulsed laser deposition with reflection high energy electron diffraction to ensure layer-by-layer and high-quality growth.

4:20pm **MI-WeA-7 Thermally Induced Magnetic Order from Glassiness in Elemental Neodymium***, **Daniel Wegner**,* Radboud University, Netherlands **INVITED**

I will present results from our most recent spin-polarized scanning tunneling microscopy (SP-STM) study of single crystalline elemental neodymium (Nd) metal, which is a self-induced spin glass in its ground state [1]. Temperature in thermodynamics is synonymous with disorder, and responsible for ultimately destroying ordered phases. We found an unusual magnetic transition where, with increasing the temperature, long-range multi-Q magnetic order emerges from the glassy state [2]. Using temperature-dependent SP-STM, we characterized the local Q order in the spin-Q glass phase and quantified the emergence of long-range multi-Q order with increasing temperature. We developed two distinct analysis tools, which enable the quantification of the glass transition temperature, based on measured magnetization images. We compared these observations with atomic spin dynamics simulations, which reproduce the qualitative observation of a phase transition from a low-temperature spin glass phase to an intermediate ordered multi-Q phase. These simulations trace the origin of the unexpected high temperature order in weakened frustration driven by temperature-dependent sublattice correlations. Our findings constitute an example of order from disorder and provide a rich platform to study magnetization dynamics in a self-induced spin glass.

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5:00pm **MI-WeA-9 Designing Antiferromagnetic Domain Landscapes via Focused Ion Beam Irradiation***, **Fabian Samad**,* Helmholtz-Zentrum Dresden - Rossendorf, Germany*; G. Hlawacek,* Helmholtz Zentrum Dresden-Rossendorf, Germany*; L. Koch,* Technische Universität Chemnitz, Germany*; X. Xu,* Helmholtz Zentrum Dresden-Rossendorf, Germany*; O. Hellwig,* Helmholtz-Zentrum Dresden - Rossendorf, Germany

Layered thin film synthetic antiferromagnets (SAFs) are highly promising candidates for future technological applications, particularly in nanomagnetism and spintronics [1]. Their magnetic properties can be easily tuned by changing the individual layer-thicknesses and also further manipulated post-deposition by applying magnetic fields or electric currents [2]. Antiferromagnetic domains in SAFs are of specific interest, as they possess strongly desirable properties, such as high stability against external magnetic fields, and large domain wall velocities [3]. However, due to the absence of a net magnetization, the deterministic creation of microscopic SAF domains is challenging [2,4].

In this project, we show that ion beam irradiation can be used to 'write' complex microscopic SAF domain patterns [5]. For this, we employ a nanometer-focused He+ ion beam, which intermixes the layer interfaces, thus changing the local magnetic properties in a controlled manner. We report highly tunable magnetic and magnetoresistive behavior of the various SAF domain patterns in the presence of externally applied magnetic fields and electric currents.

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Nanoscale Science and Technology Division
Room 304 - Session NS1+BI-WeA

Nanopore Sensing and Fabrication, Operation and Metrology of Biodevices

Moderators: David Czaplewski, Argonne National Laboratory, **Georg Fantner**, EPFL, Switzerland

2:20pm **NS1+BI-WeA-1 Single Cell and Single Molecule Biophysics with Glass Nanopores***, **Georg Fantner**, A. Radenovic, S. Leitao, V. Navikas, B. Drake,* EPFL, Switzerland **INVITED**

Scanning ion conductance microscopy (SICM) has been around for decades, yet it has not received as much attention as other forms of scanning probe microscopy. Recently, this true non-contact techniquehas kindled renewed interest among biophysicists and biologists because it is ideally suited for label-free imaging of fragile cell surfaces where it achieves exquisite resolution down to the nanometer regime without distorting the cell membrane. SICM uses a glass nanopipette as a scanning probe and measures the current through the glass nanopore as a proximity detection of the sample surface. The challenge to harness this technique for time resolved 3D nanocharacterization of living cells lies in the relatively slow imaging speed of SICM. In this presentation I will show how we apply what we have learned from high-speed AFM to the field of SICM. By reengineering the SICM microscope from the ground up, we were able to reduce the image acquisition time for SICM images from tens of minutes down to 0.5s while extending the imaging duration to days.

SICM, however, is much more versatile than just an imaging tool. I will also discuss our recent results using SICM as a single molecule characterization tool. We term this method scanning ion conductance spectroscopy (SICS). Using capillaries with exceptionally small nanopores, we are able to detect and manipulate single molecules in a repeatable and high throughout manner.

3:00pm **NS1+BI-WeA-3 Ultrasensitive Nanoporous Gold Substrates for SERS Detection in Liquids or Gases***, **Issraa Shahine**, B. Humbert, J. Mevellec, M. Richard-Plouet, P. Tessier,* Nantes Université, CNRS, Institut des Matériaux de Nantes Jean Rouxel (IMN), France

The design of three-dimensionally structured, gold nanoporous membranes is described. Our aim is to design surface enhanced Raman scattering (SERS) substrates to detect very low concentrations of molecules in liquid or gaseous phases. The SERS substrates are constituted of stacked ultrathin nanoporous gold thin layers. They are obtained in a two-step process: first deposition of alternative copper and gold stacked nanolayers by magnetron sputtering, and second, chemical etching to dissolve copper, resulting in the nanoporous morphology. The obtained thin layers of gold give rise to superior surface enhanced Raman scattering (SERS) capability using 2,2-bipyridine (BP) as probe molecules for detection. The SERS intensity mapping confirm the presence of hot spots with a low detection limit down to 10^{-18} mol.L^{-1} of BP concentration. The ultrasensitivity at low concentration molecules is assigned to the effects of the localized enhanced electromagnetic fields around the nano ligaments. An additional Raman mechanism is also highlighted by µ-Surface Enhancement Spatially Offset Raman spectroscopy (µ-SESORS): gold ligaments inside nanoporous layers act as waveguides for the incident light, leading to a significant increase in the size of the active SERS area. These SERS substrates have the ability to detect low BP vapor pressure in air.

This process is a reliable method for fabricating uniform, highly reproducible and efficient SERS substrates, with a robust SERS response at extremely low detection limits.

Nanoscale Science and Technology Division
Room 304 - Session NS2+AS+EM-WeA

Scanning Probe Metrology of 1D and 2D Materials

Moderators: Maryam Ebrahimi, lakehead University, Canada, **Aubrey Hanbicki**, Laboratory for Physical Sciences

4:20pm **NS2+AS+EM-WeA-7 New on-Surface Synthesis Techniques for Creating Precise 1D Graphene Nanoribbon Heterojunctions and Device-Tunable 2D Molecular Arrays***, **Michael Crommie**,* UC Berkeley Department of Physics*; G. Dong,* University of Chicago Department of Chemistry*; J. Lischner,* Imperial College London Department of Materials, UK*; A. Zettl, P. Jacobse, Z. Wang,* UC Berkeley Department of Physics*; J. Yin,* University of Chicago Department of Chemistry*; H. Tsai, F. Liou, A. Aikawa,* UC Berkeley Department of Physics **INVITED**

Bottom-up fabrication techniques for assembling molecular nanostructures at surfaces typically exploit various surface interactions that (along with random thermal processes) can be biased toward achieving desired structural results via the clever design of molecular precursors. Great progress has been made using this approach, but surface-grown molecular structures remain plagued by random, uncontrolled processes that make complex structural control difficult. Overcoming this problem is one of the grand challenges of this subfield. Here I will discuss two new approaches to molecular surface assembly that have allowed us to improve order in surface-based nanostructures. The first involves 1D materials and utilizes a solution-based polymerization scheme combined with a new surface deposition procedure. The second involves combining molecular surface assembly with 2D field-effect transistors (FETs). The first method is focused on graphene nanoribbons (GNRs), nanometer-wide strips of graphene. Fabricating complex heterostructure sequences in GNRs remains a difficult challenge because we can't sequence GNRs the way we sequence DNA. This makes it hard to fulfill the promise of GNR-based molecular electronics because of the difficulty of fabricating GNRs composed of well-ordered segments that each have controlled properties (e.g., bandgap, doping, magnetism, optical response). We have made progress toward overcoming this challenge by using a new protecting-group-aided-iterative-synthesis strategy. This allows us to create GNR oligomers with perfectly defined monomer sequences in solution that can be deposited onto surfaces for cyclodehydrogenation using a matrix-assisted deposition (MAD) procedure. This has enabled the synthesis of GNR heterojunctions that would not be possible via other techniques. The second technique I will discuss involves the use of an "active substrate" (a graphene FET) to induce *reversible* 2D molecular assembly through a combination of Coulomb and van der Waals interactions. The trick here is to use a molecule (in our case F_4TCNQ) whose LUMO level (E_L) lies in an energy range accessible to the Fermi level (E_F) of the 2D FET. Manipulating E_F relative to E_L via the device backgate allows charge in the device to reversibly flow between substrate states and the LUMO level of adsorbed molecules. This results in unexpected mechanical responsivity of the molecules, including tunable 2D array formation and a reversible quasi-1D phase transition that we have imaged using scanning tunneling microscopy.

5:00pm **NS2+AS+EM-WeA-9 Temperature-Mediated Adsorption and Assembly of Internally Fluorinated Chevron Graphene Nanoribbon Precursors on Au(111)***, **Jacob Teeter**,* Center for Nanophase Materials Sciences, Oak Ridge National Laboratory*; M. Sarker,* University of Nebraska - Lincoln*; C. Tao, J. Huang,* Center for Nanophase Materials Sciences, Oak Ridge National Laboratory*; W. Lu, J. Bernholc,* North Carolina State University*; A. Sinitskii,* University of Nebraska - Lincoln*; A. Li,* Center for Nanophase Materials Sciences, Oak Ridge National Laboratory

The archetypical chevron-shape graphene nanoribbon (GNR) broke new ground in the on-surface synthesis of carbon-based nanomaterials with its development in 2010 by Cai *et al*[1]. Subsequent innovation predicated on this discovery introduced a wide variety of GNRs with differing shapes, edge types, heteroatomic substitutions, topological phases, and more. One drawback to studying GNRs arising from surface-assisted synthesis is the intrinsic electronic hybridization between the GNR and the surface upon which it was grown. This convolutes electronic characterization such as scanning tunneling spectroscopy (STS), but can be mitigated somewhat through tip-based manipulation of the GNRs onto an insulating layer on the surface, or by introducing a powder of solution-synthesized GNRs to a semiconducting substrate. Only recently has a method been developed - utilizing rutile $TiO_2(011)$, rationally designed fluorinated precursors, and a surface-assisted cyclodehydrofluorination reaction - to achieve bottom-up-synthesized atomically precise GNRs on such a surface[2].

In this work, we have developed more fluorinated precursors to expand the set of atomically precise GNRs grown on semiconducting surfaces and studied their assembly on Au(111) using scanning tunneling microscopy. In particular, we have produced and prototyped on Au(111) a fluorinated chevron precursor intended to yield chevron-type GNRs on TiO_2(011). With all other factors equivalent, the adsorption of the precursor is heavily dependent on the temperature of the surface of the Au(111) crystal on which it is deposited. The lack of adsorption at room temperature is in sharp contrast with the non-fluorinated precursor, which can be deposited at room temperature and post-annealed to produce GNRs in good yield. We attribute this discrepancy to interactions between the internal F atoms and the Au(111) surface, which is supported by theoretical calculations.

This research was performed at the Center for Nanophase Materials Sciences which is a DOE Office of Science User Facility.

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5:20pm **NS2+AS+EM-WeA-10 STM Study of Superconducting Film FeTe(1-x)Se(x) on Topological Insulator Bi_2Te_3*, Hoyeon Jeon*,** *W. Ko, M. Brahlek, R. G. Moore II, A. Li,* Oak Ridge National Laboratory, USA

Topological superconductors (TSCs) have attracted great attention because they can host Majorana fermions for quantum computation. Because natural TSCs are rarely found, alternative ways to make TSCs are badly needed. One of them is using proximity effect by combining two-dimensional Dirac surface states of topological insulator (TI) with s-wave superconductivity (SC) to generate localized topological Majorana zero modes in vortex cores. Here we report the epitaxial growth of SC films of FeTe(1-x)Se(x) on TI of Bi_2Te_3, their electronic structures and surface inhomogeneities of superconductivity using scanning tunneling microscope/spectroscopy (STM/STS). A variety of samples are examined with different thicknesses of superconducting layer and selenium concentrations. We expect our results to be relevant for searching for materials platforms to host topological superconductivity.

The research is supported by the U.S. Department of Energy (DOE), Office of Science, National Quantum Information Science Research Centers., the Quantum Science Center (QSC), a National Quantum Information Science Research Center of the U.S. Department of Energy (DOE).

5:40pm **NS2+AS+EM-WeA-11 Atomic-Scale Mapping of Thermoelectric Properties of Noble Transition Metal Dichalcogenides*, Saban Hus,*** *A. Li,* Oak Ridge National Laboratory*; L. Liu, Y. Chen,* Purdue University

Monolayer noble transition metal dichalcogenides with hexagonal lattice structure are predicted to be high performance thermoelectric materials at room temperature [1]. Their pentagonal counterparts promise even better performance due to the in-plane anisotropy of the lattice [2]. However, like many other features of 2D materials, their thermoelectric properties can significantly be altered by the heterogeneities in the atomically thin layers [3]. Using a scanning tunneling microscope (STM), we investigate the thermoelectric properties of both pentagonal and hexagonal noble transition metal dichalcogenide monolayers in atomic resolution. We observe that atomic-scale defects and variations in 2D layer-substrate interface create a rich thermoelectric landscape invisible to mesoscopic scale measurements. Precise control and utilization of these heterogeneities can lead to next-generation thermoelectric devices and materials for energy applications.

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* This work was supported by Center for Nanophase Materials Sciences (CNMS), which is a US Department of Energy, Office of Science User Facility at Oak Ridge National Laboratory.

Plasma Science and Technology Division
Room 305 - Session PS1+AP-WeA
Plasma Assisted Atomic Layer Etching

Moderators: Harm Knoops, Oxford Instruments Plasma Technology, UK, Eindhoven University of Technology, Netherlands, **Emilie Despiau-Pujo**, Univ. Grenoble Alpes, CNRS, LTM, France

2:20pm **PS1+AP-WeA-1 Mechanism of Isotropic Plasma Atomic Layer Etching Using Hexafluoroacetylacetone and H_2 Plasma*, Nicholas J. Chittock*,** *J. Maas, M. Merkx, W. Kessels,* Eindhoven University of Technology, The Netherlands*; H. Knoops,* Oxford Instruments Plasma Technology, UK*; A. Mackus,* Eindhoven University of Technology, The Netherlands

Interest in atomic scale processing techniques, such as atomic layer etching (ALE), is growing rapidly as accurate thickness control and low damage etching have become necessities in IC fabrication. In this work the mechanism for isotropic plasma ALE of Al_2O_3 using the diketone species hexafluoroacetylacetone (Hhfac) and H_2 plasma is investigated. This alternative process for isotropic plasma ALE could provide improved selectivity for etching metal oxides over Si-based materials.[1,2]

ALE behavior was confirmed using Al_2O_3 planar substrates. Etching is only observed when alternating between Hhfac and H_2 plasma pulses, with the EPC determined to be 1.7 Å/cycle at 350 ˚C, which is higher than the EPC observed for Hacac/O_2 plasma ALE of Al_2O_3.[2] No thickness change was observed on thermally grown SiO_2 with this ALE chemistry, indicating near perfect selectivity between Al_2O_3 and SiO_2.

This process exhibits ALE characteristics; however, the self-limiting mechanism is not fully understood. To investigate the reaction mechanism Fourier transform infrared spectroscopy (FTIR) was employed to observe the different binding configurations of hfac on an Al_2O_3 surface. Two configurations can be determined from FTIR: chelate where both oxygen atoms bind to the same metal atom, or monodentate when only one oxygen is bound.[3] Chelate is the preferred binding configuration; however, for low dose times the majority of measured hfac surface species are in monodentate configuration. It was concluded that chelate species are lost from the surface as volatile metal-diketonate etch products. As dosing continues, the monodentate coverage increases and inhibits chelate binding, and thus etching, which explains the self-limiting behavior. A H_2 plasma pulse in half-cycle B removes the adsorbed hfac, resetting the surface for the next ALE cycle.

In summary the two binding configurations of hfac adsorbates play important and distinct roles: the chelate configuration generates volatile etch products, while the monodentate configuration ensures that the etch is self-limiting. Together these reactions, combined with surface cleaning during half-cycle B, yield an ALE process for Al_2O_3 with excellent selectivity to SiO_2 and a high level of etch control.

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2:40pm **PS1+AP-WeA-2 AVS Dorothy M. and Earl S. Hoffman Awardee Talk: On the Chemical and Physical Mechanisms of Etch Product Volatilization in Plasma Enhanced Atomic Layer Etch of Silicon Nitride with Hydrofluorocarbons*, Erik Cheng*[12],** *G. Hwang,* The University of Texas at Austin*; P. Ventzek, Z. Chen, S. Sridhar,* Tokyo Electron America

Low energy ion bombardment is a key part of plasma enhanced atomic layer etch (PEALE) which may induce surface reactions unlikely to occur under thermal conditions, moving such systems far from equilibrium. These processes, however, are uniquely challenging to study both experimentally and computationally, due the critical importance of both complex, non-equilibrium chemistry at atomic length- and timescales, as well as more long-range and sustained physical effects that influence the system beyond individual reactive sites.

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[1] **PSTD Coburn & Winters Student Award Finalist**

[2] **AVS Dorothy M. and Earl S. Hoffman Awardee**

We previously presented a novel simulation approach and used it to uncover underlying mechanisms in the ion bombardment step of PEALE of silicon nitride (SiN) with hydrofluorocarbons (HFCs). The key role of two key HFCs, CF4 and CH3F, via formation of a physisorbed monolayer, their ion-induced decomposition, and the resulting differences in etch outcomes were discussed. The details of the formation of volatile etch products, however, were less understood and are the focus of this talk.

We first note that we saw no evidence of thermal volatilization. Ar ion impacts can directly cleave bonds both in the HFC precursors as well as the underlying SiN and critically perform three key functions: 1) generating active species through HFC decomposition, 2) generating active sites on the SiN surface, and 3) enabling structural rearrangement at and near the SiN surface. Through the accumulation of damage, the Si-N bonds keeping Si atoms bound to the surface are broken over time, with coordination defects often being passivated by C, H, and F. Through this, the Si becomes more weakly bound to the surface and is thus more likely to be etched. However, many volatile fragments contain at least one N atom, suggesting that it is not always necessary to cleave all Si-N bonds for volatilization to occur. This could be associated with fragment production essentially always resulting from effects of an ion impact. For fragmentation induced by a direct Ar impact, these tend to be highly chaotic processes characterized by sputtering-like behavior, often generating multiple reactive fragments in one area that combine to form a free fragment. These events may allow a variety of surface conditions to yield etch products. We also see evidence of “secondary events” where ion impact releases a small reactive ion (for example, Si-F -> Si + F) which can impact a weakly bound moiety elsewhere on the surface to form a free fragment. These events appear to be more sensitive to surface conditions. Understanding these two key volatilization pathways may be the key to unlocking far finer levels of control over the PEALE process than currently achievable.

3:00pm **PS1+AP-WeA-3 Use of Atomic Layer Etching Techniques in Todays and Tomorrows Industry*, Dominik Metzler,*** IBM Research Division, Albany, NY **INVITED**

Atomic Layer Etching and Quasi Atomic Layer Etching processes have gained a lot of traction and application throughout the last years. However, not everything described as ALE is a true atomic layer process in its strict definition. We will first discuss the use and definition of various cyclic process and compare to pulsed processes, the process regime of which can differ significantly. In a more general consideration, the approach of reactant control, as the core of ALE, is additionally employed in various other applications that are not QALE. Subsequently, we will highlight and describe specific use cases for which such processes have been explored and implemented at IBM Research in Albany. Fin patterning is a major example of QALE yielding major improvements in profile and CD control during RIE. Additionally, QALE allowed enhanced selectivity during self-aligned contact etches, crucial to its success. For S/D recess possible benefits are expected in a similar fashion. While many of the applications focus on the FEOL, there are also applications of cyclic processes, or QALE-like, in the BEOL, such as Photoresist protection and CD control.

4:20pm **PS1+AP-WeA-7 Approaches to Improve the SiO_2 to SiN_x Etch Selectivity during ALE and RIE*, Xue Wang,*** Colorado School of Mines*; R. Gasvoda, P. Kumar, E. Hudson,* Lam Research Corporation*; S. Agarwal,* Colorado School of Mines

In plasma etching, the etch selectivity of SiO_2 relative to SiN_x can be controlled by tuning process parameters such as the fluorocarbon or hydrofluorocarbon feed gas, dilution with other gases such as H_2 or O_2, and by tuning the ion flux and the ion energy distribution. Previously, we showed that selective functionalization of plasma-deposited SiO_2 or SiN_x with hydrocarbons can be used to enhance etch selectivity. Building on our previous work, using in situ optical surface diagnostics, we will show that this approach can be extended to atmosphere-exposed and partially-etched SiO_2 and SiN_x surface during atomic layer etching (ALE). In addition, we have also studied the mechanism for the enhancement in etch selectivity for SiO_2 over SiN_x by increasing the substrate temperature during reactive ion etching (RIE).

In our previous work, we demonstrated that pre-functionalization of a pristine plasma-deposited SiN_x surface with benzaldehyde accelerates the formation of a graphitic hydrofluorocarbon layer during C_4F_6/Ar plasma-assisted ALE, and lowers the loss of SiN_x prior to complete etch stop. However, after exposure to atmosphere, SiN_x forms a SiO_xN_y layer with surface –OH groups similar to SiO_2. On the other hand, partially-etched SiO_2 and SiN_x surfaces have a residual CF_x layer, which is very reactive with most hydrocarbon molecules. Herein, using in situ ATR-FTIR spectroscopy, we demonstrate this pre-functionalization approach can be extended to technologically relevant surfaces by removing the surface SiO_xN_y layer in one ALE cycle while minimizing the CF_x residue on the SiN_x and SiO_2 surfaces: this allows for selective benzaldehyde attachment to the SiN_x surface. In subsequent ALE cycles, we show that the selectivity for benzaldehyde attachment to SiN_x over SiO_2 reduces with the slow accumulation of a carbon-rich residue on both surfaces. Using in situ 4-wavelength ellipsometry, we show that benzaldehyde dosing after the 1st ALE cycle reduces the amount of SiN_x etched and increases the etch selectivity from 1.7 to 2.1 after 20 ALE cycles. If we introduce a second benzaldehyde dose after the 5th ALE cycle, which is prior to significant CF_x accumulation on SiO_2, the selectivity further improved from 2.1 to 3.4.

Finally, we also studied the mechanism for the substrate temperature dependence on the etch selectivity of SiO_2 to SiN_x during C_4F_6/Ar plasma RIE. Our in situ optical diagnostics show that increasing the substrate temperature during RIE of SiN_x from 70 to 120 °C accelerates the formation of a graphitic CF_x layer, while there was no noticeable effect over the same temperature range during RIE of SiO_2.

4:40pm **PS1+AP-WeA-8 Plasma Atomic Layer Etching of Molybdenum with Fluorocarbon and Hydrofluorocarbon*, Yongjae Kim,*** *H. Kang, H. Ha, H. Chae,* Sungkyunkwan University, Korea

Copper is widely used for interconnect lines in semiconductor devices, and the resistivity of copper is rapidly increasing as the critical dimension shrinks below 30nm. [1] Dual damascene process based on copper have reached limits due to the continuous shrinkage of critical dimensions. Semi damascene process is an alternative technique, and metal is patterned by reactive ion etching (RIE). [2] Conventional plasma etching process has limitations in uniformity, surface roughness. Atomic layer etching (ALE) process has advantages of good uniformity, smoother surfaces, and precise thickness control than conventional reactive ion etching process.

In this work, ALE process was performed for molybdenum in an inductively coupled plasma (ICP) reactor. The ALE process consists of two steps: surface modification with fluorine contained plasma and ion bombardment with Ar plasma. In the first step, the fluorocarbon layers are deposited on molybdenum surface with C_4F_8 or CHF_3 plasmas. In the second step, the modified layers are etched with ions from Ar plasma. Molybdenum ALE process was performed with changing Ar plasma bias voltage at 50~350V, and the ALE window that constant etch rate region was confirmed with bias voltage of 100~230V. Etch rate of cobalt was self-limited at the Ar plasma time of 3 minutes. The etch rate of molybdenum controlled below 1 nm/cycle. The surface roughness was compared RIE process and ALE process, and the surface roughness of the ALE process was lower than that of the RIE process.

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Keywords: Atomic layer etching, Molybdenum etching

5:00pm **PS1+AP-WeA-9 Atomic Layer Etching of Si by Surface Chlorination, Ar or He Sputtering*, Tao Li,*** *E. Miller,* IBM Research Division, Albany, NY*; S. Schmitz, P. Friddle, W. Yang,* Lam Research Corporation

Anisotropic etching of silicon with active fin heights of 45nm or greater is critical for fin patterning and continuous CMOS scaling. Tight control of fin CD and taper is critical for the device, in particular channel control. In addition, uniform etching of iso/dense features and accurate pattern transfer across various fin dimensions require Si etching to enter atomic level control. In this IBM and Lam collaborative study, we evaluated the impact of He and Ar sputter as well as silicon nitride and silicon oxide hard mask (HM) on selectivity and Si profile. We find that nitride HM tends to be less resilient than oxide HM as sputter energy increases. For both He and Ar ALE, we explored the influence of ion-angle-scattering on fin profile as well as various surface protection methods to address ion-angle-scattering side-effect. We will also examine Ar ALE at low bias.

5:20pm **PS1+AP-WeA-10 Real-Time Monitoring of Atomic Layer Etching in Cl_2/Ar Pulsed Gas, Pulsed Power Plasmas by Optical Emission Spectroscopy***, **Qinzhen Hao**, V. Donnelly,* University of Houston*; S. Nam, H. Yoon,* Samsung Electronics, Republic of Korea

Optical emission spectroscopy was used as a real-time monitor of atomic layer etching (ALE) of Si in an Ar inductively-coupled (ICP) plasma. Pulses of Cl_2 gas were repetitively injected into a continuous flow of Ar, followed by simultaneous ignition of the ICP and application of substrate rf bias power (either continuous, or rapidly modulated) for 10s. Optical emissions in the UV from Si, SiCl, $SiCl_2$, $SiCl_3$ and Ar^+, and in the far-red from Ar and Cl were monitored as a function of time during the bias period, as well in the ICP after the bias power was extinguished. By monitoring emission along a line parallel and close to the substrate surface, and operating at high Ar flow rates, and from an analysis of the time dependencies of the decays of emissions during the bias period, it is argued that emissions are mainly from the primary products sputtered by the energetic Ar ions. Products decay with different, non-exponential time signatures. Cl rapidly decays to undetectable levels early in the bias period, indicating some sputtering of Cl (and/or Cl_2) from the top surface, while Si emission decays more slowly to a nearly constant level, indicative of physical sputtering after sub-surface Cl is nearly depleted. $SiCl_2$ emissions decay to nearly undetectable levels toward the end of the bias period. SiCl emission follows a decay profile between that of Si and $SiCl_2$. Relative emission intensities increased strongly with increasing bias power (self-bias voltages of -30 to -200 V_{DC}), but only moderately with Cl_2 pulse durations (1 to 16s). The ALE products are depleted in $SiCl_2$ and especially $SiCl_3$ relative to etching with constant Cl_2/Ar flows and continuous ICP and bias powers.

5:40pm **PS1+AP-WeA-11 Self-Limited Cyclic Etching of Copper Thin Films in Hydrogen and Argon Plasmas for Copper Hybrid Bonding***, **Qi Wang**, C. Netzband, G. Gibney, S. Voronin, S. Han, S. Arkalgud, P. Biolsi,* TEL Technology Center, America, LLC*; C. Vallee,* College of Nanoscale Science and Engineering, SUNY Polytechnic Institute

Cu/Cu hybrid bonding for 3D integration relies on nanometer level control of copper pad recess depth to create proper and reliable electrical contacts. While the recess can be achieved through chemical mechanical planarization (CMP), as feature size shrinks both Cu and dielectric polish at the same rate, resulting in planar contact pads which severely limits the process window. In this work, we report the atomic layer etch (ALE) of Cu with high selectivity to silicon oxide to supplement CMP for tight recess control across the wafer. Each cycle consists of a H_2 plasma modification step followed by directional removal of the hydrogenated layer by low energetic Ar ions. Precise ion energy control was achieved by applying a DC pulse waveform at a given voltage (energy) to the target (1μs ON time and 2μs OFF time per period). In situ ellipsometry measurements reveal self-limiting removal of material at an etch rate of ~3–4 Å/cycle for the first ALE cycle. As the number of the ALE cycles increases, the amount of material etched per cycle decreases, which is due to the modification of the initial surface roughness condition. After modification of the initial surface, the Cu film is less sensitive to the H_2 plasma and leads to decrease in etch amount per cycle. This can be recovered by physical sputtering of the surface by energetic Ar ions or by introduction of an additional modification step prior to each ALE cycle, resulting in process linearity restoration. Real time mass spectral analysis of the plasma of each etch cycle demonstrates the majority of volatile by-product is in the form of CuH_x and shows excellent correlation with the ellipsometry trends. Additional surface characterization by in vacuo XPS and AFM will be discussed.

6:00pm **PS1+AP-WeA-12 Examination of Mechanisms and Processes of Atomic Layer Etching of Copper***, **Taylor Smith**,* University of California, Los Angeles*; E. Crumlin,* Lawrence Berkeley National Laboratory*; J. Chang,* University of California, Los Angeles

Copper is the primary material used for the interconnects of an integrated circuit (IC). The dual damascene process was initially developed to deposit and pattern copper due to the difficulties of using traditional dry etching techniques, but the dual damascene process is reaching its practical limits. Atomic layer etching (ALE) is emerging as a process that could help replace the dual damascene process. In this work, we examine a plasma-thermal ALE process that uses plasma modification followed by a formic acid (FA) vapor phase removal step. Ambient pressure X-ray photoelectron spectroscopy (AP-XPS) was used to examine the FA vapor exposure step in particular detail. These *in operando* measurements aided in proposing the surface reaction mechanism of the modified copper surface during the vapor phase removal.

In addition, a nitrogen plasma was used to develop an ALE process based on nitridation of the copper film. Previous ALE of copper has used oxidation as the first modification step—however, copper spontaneously oxidizes on ambient exposure, making it difficult to decouple the effects of the process from ambient exposure. On the other hand, copper nitride does not form spontaneously on exposure to ambient conditions, so all nitridation is a direct result of processing. Plasma nitridation of copper has been accomplished using an ICP reactor with a nitrogen plasma, and the resulting copper nitride film has been characterized by XPS. The copper nitride film has an approximate composition of $CuN_{0.3}$.

Plasma Science and Technology Division
Room 315 - Session PS2+SE-WeA

Atmospheric Pressure Plasmas and their Applications

Moderators: Adam Pranda, TEL Technology Center, America, LLC, **François Reniers**, Université Libre de Bruxelles, Belgium

2:20pm **PS2+SE-WeA-1 Organized DBD Streamers for Maskless Chemical and Topographic Patterning of Surfaces***, O. Polonskyi, T. Hartig,* UCSB Chemical Engineering*; J. Uzarski,* U.S. Army Combat Capabilities Development Command Soldier Center*; **Michael Gordon**,* UCSB Chemical Engineering

Current methods for plasma-based modification of material surfaces (e.g., etching; modifying adhesion, surface chemistry, or wettability; and deposition) cannot often deliver precise control over the location of treatment without extensive use of complex lithographic or photoresist masks. Dielectric barrier discharge (DBD) plasmas operating at atmospheric pressure can accomplish such surface treatments through the creation of random plasma filaments or 'streamers' where surface treatment preferentially occurs. Unfortunately, spatially random and intermittent formation of plasma streamers usually precludes precise patterning.

In this work, we demonstrate how DBD streamers can be sufficiently controlled, via self-organization (with voltage and frequency) and more specifically with topographically patterned dielectrics and raster-scanning of a single streamer, to accomplish localized and user-defined spatial treatment of various substrates without the use of lithographic masks. Spatially organized DBD steamers were used to locally modify the wettability (hydrophilic vs. phobic character) and chemistry of various material surfaces (PMMA, nylon, Teflon, glass, metals), as well as modify surface roughness and etch. Contact angle, XPS, AFM, IR and Raman mapping before and after treatment reveal that surface chemical changes occur preferentially where streamers form, and moreover, that streamer exposure can be tailored to achieve different kinds of multifunctional surfaces. Examples to be highlighted include (i) maskless etching of PMMA on Si at specific locations, (ii) creating bio-inspired chemical patterns on glass to mimic insect carapaces with differential wetting, (iii) rendering Teflon hydrophilic at precise locations, and (iv) creating surfaces with orthogonal wetting characteristics (e.g., simultaneously hydrophilic and phobic over different length scales).

3:00pm **PS2+SE-WeA-3 An Atmospheric-Pressure Microwave Plasma Source for "Chemical Waste-Free" Surface Cleaning and Anti-Corrosion Coatings***, D. Ellis,* University of Illinois at Urbana-Champaign*; D. Krogstad,* Applied Research Institute, University of Illinois at Urbana-Champaign*; M. Sankaran, **David Ruzic**,* University of Illinois at Urbana-Champaign

Metals such as steel are widely used in infrastructure, transportation, and manufacturing where they are exposed to corrosive environments. While higher grade metal alloys can have lower corrosivity, they have significantly higher cost. A potentially more cost-effective approach is to protect metals from corrosion by protective coatings. Currently, many of the best protective coatings require application through expensive dip tank processes that result in a high amount of chemical waste that can be potentially hazardous and result in significant waste remediation costs. For this reason, there is a need to develop a low-cost, low-chemical waste process to apply protective coatings to a variety of metals, including mild steel.

We have developed an atmospheric-pressure microwave plasma for the cleaning and coating of metal surfaces. By relying predominantly on gases, such as air or nitrogen, with aerosolized precursors instead of wet chemicals, chemical waste is greatly reduced. Here, we present a study of 1008/1010 mild steel. Cleaning of surfaces was demonstrated by purposefully contaminating with oil or sodium chloride. Following plasma treatment, the surfaces were characterized by Fourier transform infrared spectroscopy (FTIR) and Rutherford backscattering spectroscopy (RBS). In the case of salt, a Bresle test was also employed. We find that the plasma is very effective in removing oil, with no hydrocarbons being detected on the treated surface through FTIR measurements. Plasma treatment is also found to be capable of removing thin layers of salt, including residual salt left after rinsing surfaces with water. We have also shown that the atmospheric pressure plasma can be used to deposit nanoscale silica coatings onto the steel substrates to promote corrosion protection and paint adhesion. Films were deposited by introducing tetraethylorthosilicate (TEOS) vapor in the plasma. The film properties, including composition and thickness, were characterized by scanning electron microscopy, FTIR, and RBS. Electrochemical testing was used to determine the corrosion protection properties of the films, while accelerated corrosion testing using salt fog was used to determine the corrosion prevention capability of the film under a compromised paint barrier. Plasma-deposited silicon oxide films were found to substantially decrease corrosion.

3:20pm **PS2+SE-WeA-4 Characteristics of Ionization Wave Propagation on Variable Thickness Dielectric Substrate***, **Joshua Morsell**, S. Shannon,* North Carolina State University

The interaction of atmospheric pressure plasma jets (APPJ's) with various materials and material topologies can greatly influence an array of existing and new plasma based applications.One area of interest is the ionization waves that are generated by these plasma jets. These ionization waves provide consistent and repeatable application of fields and excited species to the target surface. The focus of this work is to study the effect of dielectric thickness on the propagation of ionization waves as they impinge upon the target surface.

The plasma source in question is an APPJ with helium as the working gas as used in [J. Jiang et al., PSST29(2020), 045023]. The work presented utilizes a nanosecond DC pulse of positive polarity. Pulse width is 500 ns with voltage ranging from 3.5-4.5 kV. Voltage and current data is collected via integrated current probe and a high voltage probe at the source head. The dielectric surfaces consist of two experimental configurations. The first is a 3-D printed stage with a metal foil ground plane. Microscope cover glass 150 micron thick is stacked on this stage to provide a dielectric surface from 0.15 – 3.0 mm thick. The cover glass is 24x24 mm. The second configuration is a 3-D printed stage where the ground plane is a 50 mm square glass plate 1.1 mm thick with conductive ITO deposited on one side. 1 mm thick microscope slides are used to make a dielectric surface of 1.1-10.1 mm thick. Both configurations have a constant gap between the source tip and dielectric surface of 10.5-11mm. A PI-MAX 3 ICCD camera is used to image the ionization wave interaction with the target dielectric. The ICCD is gated to 5 ns and a 5 ns delay time step.

For both experiments, the surface wave velocity has a strong dependence with dielectric thickness, increasing by a factor of three from 0.15mm to 1.65mm.For thicknesses greater than 1.65mm the velocity remains relatively constant for measurements out to 10mm thickness. Surface velocity ranges from 1.5-4.5*10^4 m/s. It is noted that the initial conditions for each dataset is kept constant by ensuring that the velocity of the impinging axial ionization wave is constant. Axial velocities for the fine and bulk studies are 1.88*10^5 m/s and 1.81*10^5 m/s, respectively. These results suggest a transition in electric field structure as the axial component of the impinging wave dissipates into the dielectric bulk more readily than the radial field with a maximum penetration depth that eventually saturates the velocity of the surface wave.

This work is supported as part of the Department of Energy Center for Plasma Interactions with Complex Interfaces (PICI).

5:00pm **PS2+SE-WeA-9 Synthesis and Applications of Metal Oxides NPs***, **Davide Mariotti**,* University of Ulster, UK **INVITED**

Metal oxides are an extraordinary class of materials that have found wide applicability for a number of century-defining technologies (e.g. flat-panel display, capacitors and energy storage) mainly due to their dielectric properties and chemical inertness. Doping, defect engineering, quantum confinement and extending to clusters, ternary or high entropy oxides can create disruptive materials with new or improved properties. Atmospheric pressure microplasmas represent a viable synthesis platform to achieve exceptional tuning capability therefore achieving an exquisite control of the size, composition and defects of metal oxide nanoparticles [1-4]. In this contribution we will show how microplasmas can offer a generalized methodology for the synthesis of metal oxide nanoparticles and produce very desirable opto-electronic properties. Therefore we will discuss the formation of metal oxide nanoparticles with gas-phase microplasmas as well as hybrid plasma-liquid systems [5-10]. We will further provide an overview of their application opportunities in energy-related applications as well as other disciplines [8-9]. Examples will include oxides from Ni, Cu, Mn, Sn, Co, Mo and Zn. Finally we will provide future directions at the boundaries between ordered and disordered crystal structures.

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5:40pm **PS2+SE-WeA-11 AVS Graduate Research Awardee Talk: Immobilization of Plasma Filaments in a DBD: Discharge Characterization and Patterned Coating Deposition***, **Annaëlle Demaude**[1,2], A. Remy, D. Petitjean, J. Zveny,* Université libre de Bruxelles, Belgium*; K. Baert, T. Hauffman,* Vrije Universiteit Brussel, Belgium*; E. Goormaghtigh,* Université libre de Bruxelles, Belgium*; M. Gordon,* University of California Santa Barbara*; F. Reniers,* Université libre de Bruxelles, Belgium

Dielectric barrier discharges (DBDs) can be ignited in different discharge modes: glow, homogeneous or filamentary. At atmospheric pressure, in most gases, the latter mode is more often obtained than the others. Filamentary DBDs are characterized by the presence of micro-discharge channels (filaments), which are very short-lived (few ns) and ignite randomly in the interelectrode space.[1] This can be seen as a drawback for surface functionalization/thin film deposition by DBDs, as it can lead to inhomogeneous treatments.[2] Instead of avoiding these filaments, their higher density in current and energetic species was recently exploited to locally modify surfaces. This was achieved using auto-organized filamentary DBDs or directly by immobilization of the filaments.[3,4] Using this latter method, our team has extended the concept further to the deposition of patterned thin films.[5]

In this work, control over the ignition location of the filaments has been achieved in Ar and in N_2 by texturizing one of the dielectric surfaces to locally favor the ignition of the micro-discharges. The distribution of the filaments in the discharge gap and their electrical properties were examined by high-speed camera imaging and by electrical measurements, respectively. By injecting different precursors such as propargyl methacrylate (PMA) or vanadium(V) oxide triisopropoxide in the Ar or N_2 immobilized filaments, hydrophilic/phobic patterned surfaces or crystalline vanadium oxide (VO_x) patterns were obtained, respectively. The spatial differences in chemistry, morphology, wettability (for PMA films) and crystallinity (for VO_x films) of the deposited films were investigated by micro-XPS and micro-IR analysis, by profilometry, water contact angle measurements and XRD, respectively. The properties of the deposited films and of the corresponding discharges could then be correlated.

This opens a new route for the deposition of patterned coatings in a one step-process at atmospheric pressure and could contribute to a better understanding of chemical reactions occurring in filamentary DBDs.

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[2] **AVS Graduate Research Awardee**

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6:00pm **PS2+SE-WeA-12 Maximizing Photon Flux in a Miniaturized Photoionization Detector***, **Mackenzie Meyer**, X. Huang, A. Sivakumar, X. Fan, M. Kushner,* University of Michigan

Photoionization detectors (PIDs) use wavelength specific UV and VUV radiation to selectively ionize, for example, volatile organic and inorganic compounds (VOCs and VICs). These compounds are then detected by collecting the resulting ion current. Miniature PIDs are of interest for lab-on-a-chip applications. A miniature PID has been developed in which VUV photons are produced by a pulsed He atmospheric pressure plasma generated in a double dielectric barrier discharge (DBD). Maximizing the fluence of photons that reach the analyte inlet will increase performance of the PID, lowering the detection limit or increasing speed of operation. The operation and optimization of a DBD-PID with the goal of increasing photon fluence were computationally investigated using the 2-dimensional model *nonPDPSIM*. Several strategies were identified to increase the photon fluence. For example, making the powered electrode V-shaped instead of flat increased the photon fluence, as the electric field is enhanced at the tip of the powered electrode. Using an array of powered electrodes capable of sustaining multiple streamers also increased the photon fluence, as did positioning the electrodes closer to the analyte inlet. The most substantial increase in photon fluence came from increasing the capacitance of the bounding dielectric by increasing the relative permittivity from 10 (typical of conventional fabrication materials) to 300 (for specialized materials). Increasing the capacitance of the dielectric increased the voltage drop across the plasma and stabilized the plasma filament while increasing current for a given voltage

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Quantum Information Science Focus Topic
Room 302 - Session QS+EM+MN+NS-WeA

Systems and Devices for Quantum Information

Moderators: Megan Ivory, Sandia National Laboratories, **Dave Pappas**, Rigetti Computing

2:20pm **QS+EM+MN+NS-WeA-1 Photonics-Integrated Microfabricated Surface Traps for Trapped Ion Applications***, **Megan Ivory**, W. Setzer, N. Karl, J. Schultz, J. Kwon, M. Revelle, R. Kay, M. Gehl, H. McGuinness,* Sandia National Laboratories **INVITED**

Some of the more advanced quantum systems for applications spanning clocks, sensors, and computers are based on the control and manipulation of atoms.While these atomic systems have led to promising results in laboratory systems, the transition of these devices from the laboratory to the field remains a challenge.Recently, advances in compact vacuum technology, microfabricated surface traps, and integrated photonics are paving the way toward deployable solutions.Here, I discuss ongoing efforts at Sandia National Laboratories to leverage microfabricated surface traps for low size, weight, and power (SWaP) deployable trapped-ion systems, and the unique systematics presented by these integration efforts.In particular, I present initial demonstrations of trapped ions utilizing multilayered waveguides for UV and visible/IR light and single photon avalanche detectors integrated with microfabricated surface traps.I also present characterization of heating rates and frequency shifts in these integrated devices, and an outlook for further reducing SWaP via compact vacuum systems.

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3:00pm **QS+EM+MN+NS-WeA-3 Toward Heterogeneous Quantum Networks: Interfacing Trapped Ion, Superconducting, and Integrated Photonic Qubits***, **Kathy-Anne Soderberg**, A. Paul,* Air Force Research Laboratory*; N. Barton, A. Brownell,* Murray Associates*; D. Campbell,* Air Force Research Laboratory*; C. Craft,* Technergetics*; M. Fanto, D. Hucul,* Air Force Research Laboratory*; A. Klug,* Griffiss Institute*; M. LaHaye,* Air Force Research Laboratory*; M. Macalik,* Booz Allen Hamilton*; K. Scalzi,* Technergetics*; J. Schneeloch,* Air Force Research Laboratory*; M. Senatore,* Griffiss Institute*; E. Sheridan,* National Academies of Sciences, Engineering, and Medicine*; D. Sica,* Griffiss Institute*; A. Smith, Z. Smith, C. Tison,* Air Force Research Laboratory*; C. Woodford,* Griffiss Institute **INVITED**

Effective and efficient ways to connect disparate qubit technologies is an outstanding challenge in quantum information science. However, the ability to interface different qubit modalities will have far-reaching implications for quantum computing and quantum networking. Here we present plans and progress toward interfacing trapped ion, superconducting, and integrated photonic qubits for the purpose of entanglement distribution in a quantum network. We will also discuss how this work connects to the AFRL distributed quantum networking testbed.

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4:20pm **QS+EM+MN+NS-WeA-7 Superconductor/Semiconductor Heterostructures for Quantum Computing Applications***, **Chris Palmstrøm**,* University of California, Santa Barbara **INVITED**

Superconductor/semiconductor heterostructures have potential for quantum computing applications. Coupling superconductivity to near surface quantum wells (QW) and nanowires of high spin-orbit semiconductors have allowed the observation of zero bias peaks, which can be a signature of, but not proof of, Majorana Zero Modes, a key ingredient for topological computing. These results of induced superconductivity pave the way for lithographically defined complex superconductor/semiconductor nanostructured networks necessary for quantum computation.

Our efforts have focused on developing high mobility of near surface quantum wells of the high spin-orbit semiconductors InAs, InSb and $InAs_ySb_{1-y}$. Rather than relying on post growth lithography and top down etching to form semiconductor nanostructures, we have investigated the development of shadow superconductor growth on atomic hydrogen cleaned MOVPE-grown vapor-liquid-solid InSb nanostructures and in-vacuum chemical and molecular beam epitaxy selective area grown InAs nanostructures. We have identified Sn as an alternative for Al for use as superconductor contacts to InSb vapor-liquid-solid nanowires, demonstrating a hard superconducting gap, with superconductivity persisting in magnetic field up to 4 Tesla. Further, a small island of Sn-InSb exhibits the two-electron charging effect, a clear indication of a supercurrent.

In more conventional superconductor qubits, a dramatic size reduction of the superconducting transmon devices is predicted by the development of merged element transmon devices based on superconductor/semiconductor/superconductor heterostructures. These superconductor/semiconductor/superconductor heterostructures also allow for selective control of conductance modes in planar lateral multi-terminal Josephson Junctions

In this presentation, progress in developing superconductor/semiconductor heterostructures for quantum computing applications will be presented. This will include progress in in-situ patterning and selective area growth, multi-terminal Josephson Junctions and the recent progress towards developing a Si fin based merged element transmon – the FinMET.

5:00pm **QS+EM+MN+NS-WeA-9 High Throughput Measurements of III-V Semiconductor Materials Stack of 2DEG-Based Tunable Couplers***, **Nicholas Materise**,* Colorado School of Mines*; J. Pitten,* University of Colorado at Boulder*; W. Strictland,* New York University*; A. McFadden,* National Institute for Science and Technology (NIST)*; J. Shabani,* New York University*; E. Kapit,* Colorado School of Mines*; C. McRae,* University of Colorado at Boulder

Recent success in integrating cryogenic semiconductor classical systems with superconducting quantum systems promises to reduce the room temperature classical signal processing bottleneck. Incorporating semiconductor quantum devices with superconducting ones as tunable couplers and hybrid quantum systems requires quantitative estimates of the loss introduced by those devices. We report loss measurements of the III-V semiconductor stack used in 2DEG-based gatemon qubits and couplers using a superconducting microwave cavity. Extending the high throughput, low-cost substrate measurement method to thin films grown by molecular beam epitaxy, we can investigate surface roughness losses, bulk losses, and interface losses in a single microwave package. As with our previous measurements of substrates, we perform comparison studies with CPW resonators to validate our approach.

5:20pm **QS+EM+MN+NS-WeA-10 Strong Coupling between a Superconducting Microwave Resonator and Low-Damping Magnons Using Vanadium Tetracyanoethylene Thin Films***, Q. Xu, H. Cheung,* Cornell University*; D. Cormode, H. Yusuf,* The Ohio State University*; Y. Shi,* University of Iowa*; M. Chilcote,* Cornell University*; M. Flatté,* University of Iowa*; E. Johnston-Halperin,* The Ohio State University*;* ***G. D. Fuchs,*** Cornell University **INVITED**

Hybrid quantum systems – in which excitations with distinct origin are hybridized through a resonant interaction – are attractive for quantum technologies because they enable tunability and the ability to combine desirable properties of each excitation. Here we study the hybrid excitation of a superconducting microwave resonator mode and a ferromagnetic resonance mode of vanadium tetracyanoethylene (V[TCNE]$_x$) thin films. Our work addresses a key challenge for hybrid superconducting resonator-magnon devices: the integration of a low damping thin-film material with microfabricated superconducting circuits. V[TCNE]$_x$ is a molecular-based ferrimagnet with exceptionally low magnetic damping – as low as 5×10^{-5} at room temperature. The ability to grow thin films of this material at low temperature via chemical vapor deposition and pattern it via lift-off processing enables the fabrication of integrated quantum magnon devices using this material. We couple a V[TCNE]$_x$ magnon mode to the mode of a thin-film Nb lumped-element LC resonator and demonstrate strong coupling, characterized by cooperativities in above 10^2. Characterization of this hybrid resonator-magnon system in both the frequency domain and the time domain reveals hybridization between resonator photons and magnons. This work demonstrates a pathway for scalable and integrated quantum magnonic technologies.

6:00pm **QS+EM+MN+NS-WeA-12 Role of Point Defect Disorder on the Extraordinary Magnetotransport Properties of Epitaxial Cd$_3$As$_2$***,* ***Jocienne Nelson****, A. Rice, C. Brooks, I. Leahy, G. Teeter, M. van Schilfgaarde, S. Lany, B. Fluegel, M. Lee, K. Alberi,* NREL

Three-dimensional topological semimetals host extremely large electron mobilities and magnetoresistances making them promising for a wide range of applications including in optoelectronic devices, renewable energy, and quantum information. However, the extent to which disorder influences the properties of topological semimetals remains an open question and is relevant to both the understanding of topological states and the use of topological materials in practical applications. As a particular example, epilayers of the prototypical Dirac semimetal Cd3As2 exhibit high electron mobilities despite a having very high dislocation densities.[1,2]

Native point defects are inevitable in crystalline materials and introduce long and short-range disorder potentials that will impact carrier transport behavior. To understand their role in topological semimetals, we use molecular beam epitaxy to achieve unmatched and systematic control of point defect concentrations in Cd$_3$As$_2$. By reducing the concentration of scattering point defects, we increased the mobility from 5000 to 18,000 cm2/Vs and the magnetoresistance from 200% to 1000%. We find good agreement with the guiding center diffusion model, which indicates point defects are essential to the large linear magnetoresistance in topological semimetals.[3] However, the degree of linear magnetoresistance, is found to correlate inversely with measures of disorder. Our results demonstrate the importance of engineering high quality material with dilute concentrations of point defects to optimize the magnetoresistance properties in topological semimetals.[4]

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Advanced Surface Engineering Division
Room 317 - Session SE+MN+PS+TF-WeA

Vapor Deposition Technologies and New Trends in Surface Engineering

Moderators: Jianliang Lin, Southwest Research Institute, **Filippo Mangolini**, The University of Texas at Austin

2:20pm **SE+MN+PS+TF-WeA-1 Breaking the Back-Attraction by Bipolar HiPIMS Bursts***,* ***Rajesh Ganesan,*** University of Illinois at Urbana-Champaign **INVITED**

Limiting the back-attraction of ions is crucial to increase the deposition rate in HiPIMS processing. Back-attraction can be considerably limited by bipolar plasma bursts in which a positive voltage pulse is applied instantaneously after the negative voltage pulse. Energy-resolved mass spectroscopy confirms that, in addition to the increased flux, the energy of the target metal ions travelling from the target to the substrate is also increased, as a function of positive pulse length. Amorphous carbon coatings have been deposited by bipolar HiPIMS (BiPIMS) as a case study. The increased energy of the depositing flux led to a higher density of the carbon coatings and a significant reduction in the incorporation of the sputter gas atom, argon, was observed in the coatings. Langmuir probe measurements suggest the optimum plasma density window to minimize arc generation and reduce the probability of generated arcs moving away from the target racetrack, which results in smoother coatings. BiPIMS voltage pulses of optimized length and magnitude help to coat high quality amorphous carbon coatings with excellent machining functionalities.

3:00pm **SE+MN+PS+TF-WeA-3 Experimental and Theoretical Study of the Thermal Shock Behavior of MAX Phase Thin Films***,* ***Matej Fekete****, C. Azina, P. Ondračka, L. Löfler, D. Bogdanovski,* RWTH Aachen University, Germany*; D. Primetzhofer,* Uppsala University, Sweden*; M. Hans, J. Schneider,* RWTH Aachen University, Germany

Components subjected to rapid temperature changes are prone to thermal shock, which may result in damage or catastrophic failure. Thus, thermal shock resistance is one of the performance-defining properties for an application where extreme temperature gradients are required. The thermal shock resistance can be described by the thermal shock parameter (R_T), which depends on the flexural strength, thermal conductivity, Poisson's ratio, linear coefficient of thermal expansion, and elastic modulus. In this study, these thermomechanical properties of Ti$_3$AlC$_2$ and Cr$_2$AlC MAX phase coatings are investigated by both experiment and theory. The R_T of Ti$_3$AlC$_2$ obtained through quantum mechanical predictions is in good agreement with the experimentally obtained R_T. However, for Cr$_2$AlC, the theoretical predictions result in approximately two times larger R_T than experiments. This difference may be caused by omitted spin-polarization in the calculation of the electronic part of the thermal conductivity. Correlating the studied MAX phase thin films, both experiments and theory indicate superior facture behavior of Ti$_3$AlC$_2$ in comparison to Cr$_2$AlC. This is attributed primarily to the higher thermal conductivity of Ti$_3$AlC$_2$.

4:20pm **SE+MN+PS+TF-WeA-7 Combinatorial Application of Advanced Characterization Methods to Illuminate the Role of Interfaces in Multilayer Coatings***,* ***Nina Schalk****, C. Kainz, F. Frank,* Montanuniversität Leoben, Austria*; C. Czettl, M. Pohler,* CERATIZIT Austria GmbH, Austria*; M. Tkadletz,* Montanuniversität Leoben, Austria **INVITED**

The microstructural characterization of multilayer coatings and their interfaces is challenging, especially if the layer thicknesses are only in the nm range. Within this talk, two model coatings are used to evaluate the suitability of several characterization methods for the investigation of their microstructure and interfaces on different length scales. The fine grained cathodic arc evaporated ZrN/TiAlN and the rather coarse grained chemical vapor deposited TiCN/TiC multilayer model coatings exhibit different bilayer thicknesses and layer thickness ratios and thus allow also insight into the effect of the layer thickness on coherency, grain size and strain state. Starting with methods such as scanning electron microscopy and laboratory X-ray diffraction, an overview of the coating structure and information on the average strain/stress state can be obtained. Depending on the grain size and individual layer thickness, high resolution electron backscatter diffraction allows a more detailed insight into the microstructure and strain state of individual layers. In addition, information about gradients of strain/stress across the coating thickness is accessible by cross-sectional X-ray nanodiffraction. However, for a detailed investigation of the interfaces, the application of high resolution methods such as transmission electron microscopy and atom probe tomography is indispensable, providing information about lattice misfits and related strain evolution in the layers as well as on the sharpness of the interfaces in terms of elemental distribution down to the atomic scale. The present talk highlights that for the characterization of the different multilayer systems the combinatorial application of different characterization methods is possible and reasonable.

5:00pm **SE+MN+PS+TF-WeA-9 Influence of Al-Content on Structure, Mechanical Properties and Thermal Stability of Reactively Sputtered AlTaTiVZr High-Entropy Nitride Coatings**, ***Alexander Kirnbauer***[1], TU Wien, Austria; *S. Kolozsvári,* Plansee Composite Materials GmbH, Germany; *P. Mayrhofer,* TU Wien, Austria

In the field of materials research, a novel alloying concept, so-called high-entropy alloys (HEAs), has gained particular attention within the last decade. These alloys contain 5 or more elements in equiatomic or near-equiatomic composition. Properties, like hardness, strength, and toughness can be attributed to the specific elemental distribution and are often superior to those of conventional alloys. In parallel to HEAs also high-entropy ceramics (HECs) moved into in the focus of research. These consist of a solid solution of 5 or more binary nitrides, carbides, oxides, or borides. Within this work, we investigate the structure and, mechanical properties of thin films based on the high-entropy concept, with particular emphasis on the thermal stability, dependent on the Al content in AlTaTiVZr thin films.

Therefore, AlTaTiVZr nitride coatings were reactively sputtered in a lab-scale sputter deposition facility using a single powder-metallurgically produced composite target and Al cubes placed along the racetrack to increase the Al content within the coatings. The coatings in as-deposited state show a fine-columnar growth and crystallise in a single-phase face-centred cubic (fcc) structure. The hardness of our coatings in as-deposited state is ~32.8 GPa and relatively independent on the Al-content. We studied the influence of the Al content on the thermal stability by investigating the structural evolution of our coatings by DSC and powder X-ray diffraction, as well as nanoindentation upon vacuum annealing. The study reveals a distinct influence of the Al-content on the decomposition of the solid solution into an fcc-matrix and Al-rich domains.

5:20pm **SE+MN+PS+TF-WeA-10 Ternary Transition Metal Diborides – Future Defect Engineered Protective Coating Materials?**, *A. Hirle, L. Zauner, C. Fuger, A. Bahr, R. Hahn, T. Wojcik, T. Glechner,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria; *J. Ramm, O. Hunold,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein; *P. Polcik,* Plansee Composite Materials GmbH, Germany; ***Helmut Riedl,*** TU Wien, Austria

In the progression of novel protective thin film materials, the attention for transition metal diborides (TMB_2) substantially increased during the last years. The unique strength of their hybridized covalent bonds combined with their hexagonal close-packed (hcp) structures is a big advantage and limiting factor at the same time. The related brittleness, variety of crystal structures, and stoichiometries depict significant challenges for a broad usage of these structurally imperfect coating materials. Furthermore, the formation of non-adherent and volatile oxide scales is also a major limiting factor.

Within this study, we want to address these specific challenges on various ternary model systems within group IV to VI transition metal diborides (e.g. $TM_{1-y}X_yB_{2\pm z}$ prototypes). As structural defects play a major role for the phase formation of the two characteristic hexagonal structure types (α–AlB_2 vs. ω-W_2B_{5-x}-prototype), the target composition and ionization degree within the plasma, has been systematically correlated with the deposition parameters for non-reactive DCMS and HiPIMS depositions. In addition, different alloying concepts for enhancing the ductile character – by microstructural design of imperfect grain boundary structures [1, 2] – as well as oxidation resistance – up to 1200 °C through Si alloying [3] – of these superhard ternary diborides will be discussed in detail. To describe all these relations comprehensively, we correlated the synthesis parameters with structural and morphological evolution using XRD, HR-TEM, APT, as well as micro-mechanical testing methods. Furthermore, specific aspects have also been described by atomistic modelling (DFT).

Keywords : Ternary Borides; Protective Coatings; Defect Engineering; High Temperature Oxidation;

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5:40pm **SE+MN+PS+TF-WeA-11 Influence of Interplay of Substrate Template Effects and Bias Voltage on the Microstructure of Cathodic Arc Evaporated Fcc-$Ti_{0.5}Al_{0.5}N$ Coatings**, ***Michael Tkadletz,*** *N. Schalk, H. Waldl,* Montanuniversität Leoben, Austria; *B. Sartory, J. Wosik,* Materials Center Leoben Forschung GmbH, Austria; *C. Czettl, M. Pohler,* CERATIZIT Austria GmbH, Austria

Ever since the implementation of hard coatings as wear protection for cutting tools, their microstructural design has been of major interest. While the effect of the deposition parameters, such as the applied bias voltage or the substrate temperature, on the microstructure are frequently investigated and rather well understood, commonly less attention is paid to the used cemented carbide substrates. Yet properties like their phase composition and carbide grain size significantly influence the resulting coating microstructure. Thus, within this work substrate template effects are studied on fcc-$Ti_{0.5}Al_{0.5}N$ coatings grown by cathodic arc evaporation onto cemented carbide substrates with different WC grain sizes. A systematic variation of the bias voltage resulted in coarse, intermediate and fine grained coating microstructures, which revealed substrate template-based coating growth at low bias voltages and bias dominated coating growth at high bias voltages. In addition, a strong influence of the applied bias voltage on the resulting preferred orientation of the deposited coatings was observed, providing the basis to tailor the texture to 100, 110 or 111. Elaborate X-ray diffraction and electron microscopy studies contributed to gain further understanding of the substrate template effects and revealed that implementation of a suitable baselayer offers the possibility to effectively prevent any influence of the used substrate on the microstructural evolution of the coating. Supplementary micromechanical experiments illuminated the impact of microstructure, template and non-template based coating growth on the obtained mechanical properties. The obtained results set the fundament to implement tailored microstructures with designed gradients of crystallite size, preferred orientation and consequently mechanical properties, which, as required, either utilize substrate template effects or avoid them.

6:00pm **SE+MN+PS+TF-WeA-12 Super Hard High Temperature TaC-Based Superlattice Protective Coatings Prepared by Magnetron Sputtering**, ***Barbara Schmid,*** TU Wien, Austria; *S. Kolozsvari,* Plansee Composite Materials GmbH, Germany; *P. Mayrhofer,* TU Wien, Austria

Transition metal carbides belong to ultra-high temperature ceramics (UHTC) and are particularly valued for their high thermal and mechanical stability as well as melting points of even above 4000 °C. Therefore, those materials are especially interesting for the application as protective coatings. However, a considerable limitation of these materials is their high inherent brittleness. Inspired by the success of nanolayered superlattice architecture—shown to enhance both hardness and toughness of transition metal nitrides like TiN/CrN or TiN/WN—we developed superlattice films based on TaC. These combinations are motivated by ab initio density functional theory calculations exhibiting large and small shear modulus and lattice parameter misfits. Our coatings are prepared via non-reactive DC and pulsed DC magnetron sputtering using binary carbide compound targets. In our study, we want to compare TaC-based superlattice systems and investigate the influence of the superlattice architecture on material characteristics like mechanical, thermal and electrical properties. Apart from nanoindentation and micromechanical cantilever testing for hardness and fracture toughness, material stability at elevated temperatures as well as thermoelectrical properties are being characterized.

Surface Science Division

Room 319 - Session SS+AS-WeA

Memorial Session in Honor of Patricia Thiel I

Moderators: Alex Belianinov, Oak Ridge National Laboratory, **Dapeng Jing**, Iowa State University

2:20pm **SS+AS-WeA-1 Assembly and Stability of Metal Nanoclusters at Surfaces: Modeling Inspired by Thiel-Group STM Studies**, ***Jim Evans,*** *Y. Han,* Iowa State University; *D. Liu,* Ames Laboratory USDOE; *K. Lai,* Fritz Haber Institute of the Max Planck Society, Germany **INVITED**

STM studies by the Thiel group have characterized diverse non-equilibrium growth shapes for 2D metal nanoclusters (NCs) formed by deposition on

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[1] **2021 ASED Young Investigator Awardee**

strongly-binding metal surfaces, as well as the NC size and spatial distributions [1,2]. More recent work also considered deposition on a weakly-binding graphite substrate, producing not just supported 3D NCs, but also NCs intercalated beneath the top graphene layers [3]. These observations have guided development of predictive atomistic-level modeling of all aspects of the nucleation and growth process. For example, this modeling successfully captures the growth morphologies of individual NCs: fractals for limited periphery diffusion, height selected NCs due to quantum size effects; core-ring vs intermixed alloy structures for co-deposition; star-fish NCs on 5-fold quasicrystal surfaces; "squeezed" 3D NCs for intercalation, etc.

These arrays of supported metal NCs are metastable, and thus coarsen to fewer, larger NCs (reducing the energy cost of broken bonds at NC peripheries) on a time-scale typically significantly longer than that for deposition. In contrast to the expected Oswald Ripening (OR), the Thiel group showed for metal(100) homoepitaxy, coarsening was dominated by 2D NC diffusion and coalescence, i.e., Smoluchowski Ripening (SR) [4]. This observation has prompted extensive theory development for the NC size-dependence of diffusion (as this controls SR kinetics). For metal(111) homoepitaxy where OR occurs, the Thiel group explored the dramatic acceleration of OR due to even trace amounts of chalcogens due to the formation of metal-chalcogen complexes [4]. This work has also prompted extensive recent theoretical development.

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2:40pm **SS+AS-WeA-2 Stability and Dynamics of Sulfur-Metal Complexes on Coinage Metal Surfaces*, Da-Jiang Liu,*** Iowa State University **INVITED**

Interactions between sulfur and other chalcogen atoms and metal surfaces are critical in areas such as heterogeneous catalysis, self-assembled monolayers, and 2D materials. Over the last decade, Prof Thiel's research group has conducted a systematic survey of adsorption of sulfur on various high symmetry surfaces of Cu, Ag, and Au using low temperature STM. A rich variety of sulfur-metal surface complexes have been observed, depending on the type of metal, the coverage of sulfur, and the surface orientation.
Identification of those complexes is facilitated by density functional theory (DFT) studies, which provide information regarding energies, geometries, and simulated STM images.
Those sulfur-metal complexes are crucial for mass transport that affects surface morphology. Molecular dynamics simulations using machine learning potentials trained from DFT calculations provide insights regarding the the role sulfur plays in enhancement of surface mass transport.

3:00pm **SS+AS-WeA-3 The Atomic of Structure of Surfaces: From Vacuum to Gas and Liquid Environments*, Miquel Salmeron,*** Lawrence Berkeley National Laboratory **INVITED**

The development of spectroscopies (XPS, XAS) and microscopies (STM) that can operate in ambient gas pressures has revealed that the structure of material surfaces depends strongly on the environmental conditions of gas composition, pressure and temperature. Experiments have shown that adsorption of atoms and molecules can substantial restructure surfaces that are otherwise stable under vacuum conditions. Restructuring is manifested in the breaking on the initially flat crystalline surface by formation of nanoclusters from atoms detached from steps and other defects. In the case of alloys, adsorbed species change the surface stoichiometry by inducing segregation of alloy components. This restructuring is important because the catalytic activity and selectivity of catalyst surfaces can be strongly modified.

I will discuss the possible generality of this phenomenon by analyzing cases where atomically flat surfaces of many transition metals undergo such changes in the presence of CO even at cryogenic temperatures, while others remain unchanged

4:20pm **SS+AS-WeA-7 The Influence of Alloying on Surface Kinetics*, Karina Morgenstern,*** Ruhr-Universität Bochum, Germany **INVITED**

The physical properties of nanoscale systems differ from those of macroscopic systems, making them attractive candidates to tune the electronic or optical properties of matter. However, nanostructures are thermodynamically only metastable, altering their shape and thus their properties even at room temperature [1]. Patricia Thiel and coworkers extended this work from vacuum to coarsening in the presence of chalcogens [2] and pioneered work for heteroepitaxial systems [3]. Following the latter, we use Ag/Cu(111) that serves, at a lattice mismatch of 13%, as a representative for a large deposit on a substrate with a small lattice constant. This large difference influences growth, induced growth, and decay of Ag nanoislands on Cu(111) as revealed by variable temperature scanning tunneling microscopy [3]. For natural growth, the dimensionality of the structures depends on temperature. A layer-by-layer growth at low temperature suggests that low-temperature growth might be an effective way to overcome the kinetic limitations of the step edge barrier for forming smoother interface layers. Similar, but not identical clusters can be induced from a 2D gas by scanning the surface at elevated voltages. The higher temperature islands exhibit a misfit dislocation pattern, which influences their decay. We relate specifically stable, magic island sizes to the complexity of the heteroepitaxial decay. Even more unusual is the decay of Cu-Ag core-shell islands, for which we discuss two qualitatively different types of decay mechanisms [5]. The implication of the kinetics. for the physicochemical properties of the nanoparticles are discussed in this talk.

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5:00pm **SS+AS-WeA-9 Cluster Superlattice Membranes*, Thomas Michely,*** University of Cologne, Germany **INVITED**

Cluster superlattice membranes are a new type of a 2D material consisting of a two dimensional (2D) hexagonal lattice of similar-sized nanoclusters sandwiched between a single-crystal 2D layer and an embedding matrix material. The fabrication process involves three main steps, the templated self-organization of a cluster superlattice on the moiré of a 2D layer with a metal substrate, conformal embedding in a matrix, and subsequent lift-off from the metal substrate. The mechanical stability provided by the matrix of nm-thickness makes the membrane stable as a free-standing material and enables transfer to other substrates. The fabrication procedure is proposed to be applicable to a wide variety of cluster materials and cluster sizes from the single-atom limit to clusters of a few hundred atoms, as well as to several 2D layer/host matrix combinations.

In this talk we will exemplify the cluster superlattice membrane concept for Ir clusters on graphene or a monolayer of hexagonal boron nitride and embedded in a carbon matrix. The membrane fabrication process is characterized step-by-step using scanning tunneling microscopy and spectroscopy, x-ray photoelectron spectroscopy, optical and transmission electron microscopy, as well as Raman spectroscopy.

The versatility of the membrane composition, its mechanical stability, and the simplicity of the transfer procedure make cluster superlattice membranes a promising material in catalysis and magnetism, for which potential applications are outlined.

The contributions of Pantelis Bampoulis, Tobias Hartl, Moritz Will, Stefan Schulte, Kai Kämper, Davor Čapeta, Rajendra Singh, Daniel Scheinecker,

Virginia Boix de la Cruz, Sophia Dellmann, Paolo Lacovig, Silvano Lizzit, Boris V. Senkovskiy, Alexander Grüneis, Marko Kralj, Jan Knudsen, and Jani Kotakoski to this work are gratefully acknowledged.

5:40pm **SS+AS-WeA-11 High Quality 2-D Materials Characterized Paradoxically from Broad Diffraction Features.***, **Michael Tringides**,* Iowa State University and Ames Laboratory US-DOE **INVITED**

Paradoxically a very broad diffraction background, named the Bell-Shaped-Component (BSC), has been established as a feature of graphene growth. Recent diffraction studies as a function of electron energy on Gr/SiC have shown that the BSC is not related to scattering interference. The broad background is in-phase with the Bragg component of both the (00) and Gr(10) spots. Instead textbook diffraction states it should be out-of-phase, since it should originate from destructive interference between adjacent terraces[1]. Additional experiments were carried out as a function of temperature over the range 1200° C-1300° C that single-layer-graphene (SLG) grows. Quantitative fitting of the profiles shows that the BSC follows the increase of the G(10) spot, proving directly that the BSC indicates high quality graphene[2]. The BSC has been also in graphene on metals including Gr/Ir(111)[3]. Recent experiments also show that the BSC is present in h-BN films grown on Ir(111)[3,4]. Its presence in such a wide range of 2-materials suggests its origin must be general and fundamental related to the unusual single layer uniformity common to these widely varying films. One possible explanation of the BSC relates to electron confinement within a single uniform layer which suggests that the BSC is an excellent measure of their uniformity. The confinement of the graphene electrons and the corresponding spread in their wavevector has been seen with ARPES[5]. The transfer of the large momentum spread to the diffracted electrons requires better theoretical understanding of the graphene electron-beam electron interaction.

On a personal note this was one of the last but very enjoyable scientific interactions I had with Pat. From the very beginning she was very enthusiastic and insightful about the problem. This was particularly important because the results were unintuitive and unexpected. This is a statement to her unusual combination of strengths: an extraordinary scientist with deep insights and a warm communicative friend.

In collaboration with P.A.Thiel (deceased), M. Horn von Hoegen , E. H. Conrad.

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Thin Films Division
Room 316 - Session TF1+AP-WeA
Manufacturing and Scale-Up of CVD and (Spatial) ALD

Moderators: Joe Becker, Kurt J. Lesker Company, **Marceline Bonvalot**, Grenoble Alpes University, France

2:20pm **TF1+AP-WeA-1 Optimizing Vapor Delivery of a Nickel Diazadienyl Complex for Nickel Metal Atomic Layer Deposition***, J. Maslar, **Berc Kalanyan**,* NIST-Gaithersburg*; V. Dwivedi,* NASA*; D. Moser,* EMD Electronics

Nickel metal films find applications in numerous areas, including microelectronics and heterogeneous catalysis.In the case of microelectronics in particular, a nickel metal thermal deposition process that can produce high-purity, thin, conformal films at low deposition temperature is highly desirable.Atomic layer deposition (ALD) is widely used to deposit thin, conformal films when suitable precursors are available.However, because nickel is an electropositive metal, many of the combinations of reducing agent and metal precursor classes employed in more traditional metal thermal ALD processes are not suitable for Ni ALD.In contrast, transition-metal diazadienyl complexes represent a class of precursors that has been used successfully for metal thermal ALD, with the deposition of nickel films achieved using bis(1,4-di-*tert*-butyl-1,3-diazadienyl)nickel [$Ni(DAD)_2$].[1]A complicating factor in the reproducible deposition of nickel metal films with $Ni(DAD)_2$ is that this precursor is a solid at typical delivery temperatures and, in general, delivering a constant flux of a solid precursor can be difficult.Flux variations may not be an issue for an ideal ALD process unless the total precursor dose is insufficient to saturate all surface reactive sites, however, it is not clear what delivery conditions are necessary to provide consistently saturating $Ni(DAD)_2$ doses.The goal of this investigation is to optimize $Ni(DAD)_2$ delivery for nickel ALD and to identify any factors that may lead to irreproducible delivery.To achieve this goal, the dependence of the flux of both $Ni(DAD)_2$ and the DAD ligand (the primary decomposition product under the conditions of this study) on delivery conditions was characterized.The flux of each species was measured simultaneously using a two-channel gas analyzer which employed a broadband ultraviolet-visible source, a beam splitter, bandpass filters for wavelength isolation, and avalanche photodiode detectors.While the results of this investigation specifically apply to $Ni(DAD)_2$ delivery, it is expected that these results should also provide insight into optimizing delivery of other transition-metal diazadienyl complexes, as well as solid precursors in general.

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2:40pm **TF1+AP-WeA-2 Mechatronic Spatial Atomic Layer Deposition: Model-Informed Design for Scalable Manufacturing***, **Daniel Penley**, T. Cho, O. Trejo, K. Barton, N. Dasgupta,* University of Michigan, Ann Arbor

Spatial atomic layer deposition (SALD) holds promise to address the large-scale manufacturing needs of interfacial engineering at the nanoscale. However, the many SALD systems are limited in their ability to tune and dynamically control the full range of key process parameters, such as the depositor head and substrate gap size and parallel alignment. This lack of mechatronic control limits the ability to examine the coupled chemical, thermal, and transport phenomena as a function of SALD process parameters. Additionally, there have been several previous efforts to computationally model the SALD processes. However, there is a general lack of experimentally-validated models to verify the effects of systematically tuning the multitude of process parameters during SALD growth.

Herein we describe a customized SALD system that enables mechatronic control of key process parameters. A showerhead depositor design effectively delivers precursor to the substrate surface while stepper motors and capacitive probes maintain gap size and parallel alignment through multiple axis tilt and closed-loop feedback. Precision motorized stages control the substrate velocity and positioning, *in situ* monitoring actively controls the gas flow rates, and a thermal management system controls process temperature. We developed a three-dimensional COMSOL Multiphysics model to understand the pressure, velocity, and concentration fields of the precursor gas flow within the system geometry. The capability to tune process parameters both physically and digitally allows for the unique ability to experimentally validate and parameterize the computational model to gain further insight into the otherwise difficult to access process area of close-proximity SALD. Using this linked experimental and modeling approach, we demonstrate the model’s ability to predict resulting films from the mechatronic SALD system. With the experimentally-validated model and system, we present a study of the impact of SALD process parameters on the uniformity and quality of deposited SALD films. We then broaden our findings to discuss design implications SALD system design on the manufacturing tradeoffs of quality-throughput-cost-sustainability.

3:00pm **TF1+AP-WeA-3 Atmospheric Pressure Spatial ALD of Al-Doped ZnO: Co-injection vs. Supercycles***, **Mike van de Poll**, B. Macco, E. Kessels,* Eindhoven University of Technology, Netherlands

Atmospheric pressure spatial atomic layer deposition (ALD) is particularly interesting for high volume, low cost applications, because of its exceptionally short deposition times compared to temporal ALD.

For doped and compound materials, such as transparent conductive oxides, the electrical and optical properties are typically closely related to their composition. This makes accurate compositional control essential for high quality films. Spatial ALD of doped and compound materials generally follows one of two approaches. Supercycles can be formed by alternating two ALD cycles with different precursors, where the ratio between both cycles determines the composition of the deposited film. Alternatively, in the so called co-injection approach, the precursors can be dosed simultaneously. Here, the composition is determined by the precursor flows ratio.

In this work, ZnO:Al thin films were deposited using spatial ALD, with diethylzinc (DEZ) and dimethylaluminum isopropoxide (DMAI) as zinc and aluminum precursors, respectively, and H_2O as co-reactant. The supercycle and co-injection approaches were used, and the cycle ratio and mixing ratio were varied to alter doping concentrations. The films were capped with a layer of Al_2O_3 to shield from the ambient, and to mitigate hydrogen effusion. Electrical and optical properties of the samples as-deposited, and after stepwise anneal, were extensively studied.

Co-injection and supercycles resulted in the successful deposition of ZnO:Al films with optical and electrical properties (e.g., resistivity = 1.73 mΩcm, mobility = 9.6 cm^2/Vs, carrier concentration = $3.75 \cdot 10^{20}$ cm^{-3}) similar to temporal ALD ZnO:Al. Furthermore, the extensive study of these approaches led to identification of their advantages and disadvantages. Co-injection results in films with low resistivity as-deposited, due to homogeneous distribution of dopants. However, obtaining low Al doping levels can be practically challenging because low DMAI flow is required. Meanwhile, supercycles give precise compositional control by changing the cycle ratio, but result in dopant planes with low doping efficiency, and post-deposition anneal is required. After annealing the results are similar to co-injection.

Currently, our work focusses on the innovative approach of co-injection supercycles. Here, pure DEZ and co-injection DEZ/DMAI cycles are alternated, allowing additional compositional control by tuning both the DMAI flow during the doping cycle, and the cycle ratio. With co-injection supercycles we aim to combine the advantages of both dosing approaches. Initial films have been deposited and the full study will be presented at the conference.

3:20pm **TF1+AP-WeA-4 Manufacturing of ALD-enhanced Li-ion Batteries via Particle ALD Coatings And R2R ALD on Separators**, ***Markus Groner***, *A. Dameron, B. Hughes, D. Lewis, J. Keene, M. Martinez, J. Burger, M. Rodgers, J. Ragonesi,* Forge Nano; *J. Li,* Oak Ridge National Laboratory, China; *W. Steenman, K. Livingston,* Oak Ridge National Laboratory

ALD processing equipment for coating anode, cathode, and separator materials at scale has been developed to demonstrate ALD-enhanced Li-ion battery manufacturing. The promising performance enhancements seem previously in coin cells for ALD coated anode and cathode powders are now being validated in pouch cells. Thin ALD coatings can stabilize graphite and NCM materials, yielding improved capacity retention and rate performance, especially at higher voltages. Particle ALD coating tools are available for coating powders at the tons-per-day scale, both in semi-batch and continuous ALD versions. Additionally, ALD coatings on separators enhance electrolyte wetting and thermal stability, which should lead to improvements in the time & energy intensive filling/formation/aging steps as well as safety. A true roll-to-roll ALD tool for coating separators with alumina ALD films has been designed and built. Over the next year, this R2R tool will be integrated with a slitter and a pouch cell stacker. The performance improvements of the ALD-coated anode and cathodes, combined with the benefits of R2R ALD-coated separator, promise reductions in the cost/time/energy of battery manufacturing via ALD-enhanced Li-ion batteries.

Thin Films Division
Room 316 - Session TF2-WeA
Solution Based and Graphene or Polymer Deposition Techniques

Moderators: Parag Banerjee, University of Central Florida, **Mark Losego**, Georgia Institute of Technology

4:20pm **TF2-WeA-7 The Truth About Graphene - Where Is It and Why It Is Taking This Long to Get Here**, *M. Baraket,* ***Michael Stanford,*** General Graphene Corporation

Graphene is a monolayer of sp^2-bonded carbon atoms assembled in a honeycomb lattice structure that has attracted incredible attention for its many promising properties. It has been said that Graphene can do anything you need - except get out of the laboratory. The CVD-grown large area graphene has yet to become useful outside the laboratory due to its cost which is usually well over $10,000 dollars per square meter. Consequently, graphene's accessibility has been severely restrained with virtually no chance to integrate into industrial applications requiring high product volumes. To address this, General Graphene has scaled-up the graphene growth using an atmospheric pressure CVD process to produce cost effectively truly large-scale mono and multilayers graphene. This led us to produce different graphene types from polycrystalline graphene grown on polycrystalline copper to single oriented grown on single oriented copper to various forms of multilayer. All this can be produced with a single machine with production rates exceeding >30,000 m^2/year. Now that costs and production are in line with industrial applications – the final step is to integrate graphene into targeted applications where its unique properties and abilities provide significant competitive advantages. On the other hand, there is not a single transfer method that works for all applications. This leads to a variety of transfer methods, each with their strengths and weaknesses.

In this talk a brief history of graphene will be presented with emphasis on the challenges faced in growth and transfer along with current state-of-the-art applications with real-world performance and cost data.

4:40pm **TF2-WeA-8 Initiated Chemical Vapor Deposition (iCVD) for Shape-Programmed Polymer Nanoparticles**, ***Rong Yang,*** Cornell University

Shape-programmed polymer nanoparticles (PNPs) represent a critical opportunity to advance research in small molecule drug delivery, self-assembly for soft robotics, and metamaterials with emergent properties. Extant techniques like emulsion polymerization commonly used to synthesize PNPs primarily produce particles that are spherically shaped. To achieve non-spherical PNPs, time-consuming solution-based protocols are commonly required, along with additional fabrication and purification steps. The limited selection of monomers, restricted by their solubility, leads to a narrow range of PNP shapes and chemistries, whose deployment is further hindered by the laborious and costly synthesis. Here we present the rapid synthesis of shape-programmed PNPs without the need for nano/microfabrication, enabled by two fresh strategies revolving around initiated chemical vapor deposition (iCVD) polymerization.

The first strategy is a novel template- and solvent-free technique we recently developed, namely condensed droplet polymerization (CDP), which delivers unprecedented flexibility in PNP synthesis. With CDP, particle sizes and dimensions could be varied continuously, from sub-10 nm to above 1 µm. As a proof-of-principle, we demonstrated the synthesis of polymer nanodomes (hydrophilic, hydrophobic, cross-linked, fluorinated, biocompatible) within minutes (seconds for polymerization).

The second strategy is to leverage structured liquids, such as liquid crystals, as templates for the polymerization with reactants, i.e., monomers and initiators, delivered with picomole precision in the vapor phase. The precise delivery of reactants allows polymerization to proceed without disturbing the dynamic structures of liquid templates. A variety of shapes, including nanospheres, domes, disks, and porous networks could thus be obtained using a single technique.

These novel strategies build upon an existing manufacturing instrument, i.e., iCVD, and hence can be scaled down for decentralized manufacturing, or scaled up for industrial production in semi-continuous roll-to-roll fashion. The ability to manufacture shape-programmed soft materials is critical for advancing a wide cross-section of applications ranging from soft robotics to tough yet injectable implants.

5:00pm **TF2-WeA-9 Synthesis, Properties and Applications of Donor-Acceptor Conductive Polymers by Oxidative Chemical Vapor Deposition**, ***Marek Charyton***, *N. Boscher,* Luxembourg Institute of Science and Technology (LIST), Luxembourg

Conjugated polymers (CPs) have recently gained great scientific attention as promising materials for next generation of photo(electro)catalysts due to their unique physical (thermal and chemical stability, light resistance), optical (broad and intensive absorption) and electronic properties (redox potential, excellent conductivity). Many strategies to tailor the photocatalytic performance of CPs was studied, focusing on tuning band gap or enlarge the separation of electron-hole pairs. Alternatively, the photocatalytic properties of CPs can be also modified by their molecular design. Alternating electron-rich (donor, D) and electron-poor (acceptor, A) units along the polymer's backbone highly impact conductivity and reactivity of the designed polymers. However, to enable large-scale fabrication of optoelectronic, organic materials conductive polymers such as CPs have to be synthetised in straight-froward and low-cost processes. Herein, we propose Oxidative Chemical Vapor Deposition (oCVD) as a method that fulfils these requirements. This solvent-free technique allows to form polymers *via* vapor phase deposition directly on the desired surface thus, reducing significantly use of chemical reagents during the process. Moreover, in contrast to conventional liquid methods such aspalladium catalyzed polymerization solubilizing groups are not needed therefore, the method is not limited to only sufficiently soluble monomers. Despites the many merits of oCVD the method have not been widely studied yet. Up to date, the monomers studied in the polymerization *via* oCVD were limited to single electron rich systems like thiophene, EDOT, pyrrole, porphyrins etc.. This presentation describes the development of conductive donor-acceptor conjugated polymer obtained using oCVD method. The conductivity of the obtained thin films was tuned up to 9.75 S cm^{-1} by modification of reaction conditions. Further optical, electrochemical properties and photo(electro)catalytical performance of obtained materials were studied showing the fabricated layers can be used as efficient catalysts for water splitting reaction.

5:20pm **TF2-WeA-10 Effect of doping and annealing on the Optical and Magnetic properties of Sol-Gel deposited NiZn Ferrite films***, **Roni Paul**, S. Kothapally, J. Abu Qahouq , S. Kotru,* The University of Alabama

Ferrite films are of interest in high-frequency applications because of their high resistivity, lower eddy current losses, and better magnetic properties compared to metal alloy films. In this work we investigated the effect of doping (Cu and Co) and annealing on the optical and magnetic properties of NiZn Ferrite films. Films with three different compostions $Ni_{0.5}Zn_{0.5}Fe_2O_4$,$Ni_{0.35}Cu_{0.2}Zn_{0.45}Fe_2O_4$and $Ni_{0.35}Co_{0.2}Zn_{0.45}Fe_2O_4$ were deposited on quartz substrate using the sol-gel technique. The grown films were annealed at 500 and 800°C in a Rapid Thermal Annealing (RTA) furnace. The structural, optical, and magnetic properties of undoped and doped films were studied as a function of annealing temperature using X-ray Diffractometer (XRD), UV-VIS spectrophotometer, and Vibrating Sample Magnetometer (VSM), respectively. Bandgap of the materials was calculated using absorbance data collected from the UV-VIS spectrophotometer. Permeability values were extracted from the hysteresis loop. The $Ni_{0.35}Cu_{0.2}Zn_{0.45}Fe_2O_4$film annealed at 800°C exhibited maximum permeability (33.94) with minimum bandgap (2.5eV). The results will be presented.

5:40pm **TF2-WeA-11 A Scalable Method for Rare Earth Oxide Thin Films by Chemical Solution Deposition***, **Daniel Rodriguez**, A. Edgar, D. Vodnik, I. Usov,* Los Alamos National Laboratory

Rare-earth metals are a diverse group of elements with properties found nowhere else on the periodic table, and when in their oxidized forms, they exhibit unique traits, such as corrosion resistance to molten metals. In this study, we have applied a chemical solution deposition (CSD) process for coating stainless steel (SS) with thin films of both erbia (Er_2O_3) and yttria (Y_2O_3).

The focus of this talk will discuss different approaches for depositing rare-earth oxides onto SS304/SS316 geometries by both dipping and spraying. For dipping techniques, the formation of Er_2O_3 and Y_2O_3 coatings takes advantage of metal-nitrate solution chemistry, and its transformation into metal-oxide by both thermal annealing and ultra-violet photo-curing. For spray coating (Fig.1), deposition of Y_2O_3 involves deployment of aerosols with inclusion of binding agents such that the oxide is physically stable on the substrate, but also by incorporating substrate treatments to improve its chemical bonding. The results will reflect how fine adjustments to CSD methods leads to improved adhesion strength, composition, uniformity, and reproducibility of both coating thickness and micro-structure. Last, the scalability of CSD will be explained and compared to chemical and physical vapor deposition methods.

The outcome of this work is expected to reduce cost of the metal casting process and provide direct economic and environmental impact. In addition, there are interesting fundamental questions about the properties of rare-earth materials. Therefore, by identifying materials with practical applications, more experiments can be done to further understand the underlying physics and chemistry.

2D Materials Technical Group

Room 303 - Session 2D+AS+NS+SS-ThM

2D Materials: Scanning Probe Microscopy and Spectroscopy

Moderators: Matthias Batzill, University of South Florida, **Yi-Ting Hsu**, University of Notre Dame

8:00am **2D+AS+NS+SS-ThM-1 Atomically Precise Graphene Nanoribbons for Quantum Electronics***, An-Ping Li,* Oak Ridge National Laboratory **INVITED**

An-Ping Li, Chuanxu Ma, Marek Kolmer, Wonhee Ko, Kunlun Hong, Peter Bonnesen, Alex Puretzky, Jingsong Huang, Liangbo Liang, Bobby Sumpter

Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA

Graphene nanoribbons (GNRs) possess high mobility and current-carrying capability, sizeable bandgap, long mean free path, localized spin and topological edges states [1]. These properties make them attractive candidates for quantum electronic applications. Atomically precise GNRs can be synthesized bottom-up using controlled on-surface chemical reactions from rationally designed molecular precursors [2]. The on-surface reactions of molecular precursors performed under ultra-high vacuum conditions can further be combined with scanning tunneling microscopy (STM) for in situ characterization of atomic, electronic, and magnetic properties. In this talk, I will discuss our recent progress in realizing novel quantum states in GNR heterostructures at atomic precision. First, a bottom-up approach is developed to couple graphene nanodot (GND) covalently at the edges of GNR to create quantum-well-like states for well-defined narrow-band light emission [3], which highlights a route to programmable and deterministic creation of quantum light emitters. Second, atomically precise GNRs are obtained by the on-surface synthesis approach on a model metal oxide, showing entangled magnetic states decoupled from the substrate [4]. These works illustrate that by using bottom-up synthesis—complemented by advanced microscopy and spectroscopy, as well as theory/simulation to enable atomistic level control—a rational approach to graphitic quantum electronic materials can be established with atomic precise.

The research was conducted at the Center for Nanophase Materials Sciences (CNMS), a US Department of Energy User Facility. The electronic characterization was funded by ONR grants N00014-20-1-2302 and N00014-16-1-3153.

[1] H. Wang et al., Graphene nanoribbons for quantum electronics, *Nat. Rev. Phys.* 3, 791 (2021). https://doi.org/10.1038/s42254-021-00370-x

[2] C. Ma et al., On-surface cyclodehydrogenation Reaction Pathway Determined by Selective Molecular Deuterations, Chemical Science 12, 15637 (2021). https://doi.org/10.1039/D1SC04908A

[3]C. Ma et al., Engineering Edge States of Graphene Nanoribbons for Narrow-Band Photoluminescence, *ACS Nano* 14, 5090 (2020). https://doi.org/10.1021/acsnano.0c01737

[4] M. Kolmer et al., Rational synthesis of atomically precise graphene nanoribbons directly on metal oxide surfaces, *Science* 369, 571 (2021). https://www.science.org/doi/10.1126/science.abb8880

8:40am **2D+AS+NS+SS-ThM-3 Band Gaps of Single-Layer Transition-Metal-Dichalcogenides Determined by Scanning Tunneling Spectroscopy***, **Randall Feenstra**, G. Frazier, J. Lou,* Carnegie Mellon University*; Y. Pan, S. Foelsch,* Paul Drude Institute, Germany*; Y. Lin, B. Jariwala, K. Zhang, J. Robinson,* Penn State University

Using scanning tunneling spectroscopy at a temperature of 5 K, the electronic states of single-layer MoS_2 and WSe_2, grown on epitaxial graphene, have been investigated. Data is acquired utilizing a high-dynamic-range method in which the sample-tip separation is varied as a function of the sample-tip voltage (separation is decreased linearly as the magnitude of the voltage is reduced). Resulting spectra, when normalized to constant sample-tip separation, display conductance values that range over 5 – 6 orders of magnitude above the noise level [1]. The resulting edges of the conduction and valence bands, as well as onsets of higher/lower lying bands, are clearly defined. A theory for fitting the spectra is developed in which the varying wave-vector of the electronic states is explicitly included, yielding significant improvement in the quality of the fits compared to prior work [2]. Band onset energies can be determined with an accuracy of ~20 meV [1]. However, certain features in the data remain poorly explained by the model, in particular, an apparent broadening or smearing of the band edges which is 5x larger than that given by any instrumental effect (kT broadening together with modulation voltage of the measurement). Tentatively, this additional broadening is attributed to tip-induced band bending. Results of fitting which includes this effect will be described.

[1] R. M. Feenstra, G. R. Frazier, Yi Pan, St. Fölsch, Y.-C. Lin, B. Jariwala, K. Zhang, and J. A. Robinson, J. Vac. Sci. Technol. A **39**, 011001 (2021).P. Mårtensson and R. M. Feenstra, Phys. Rev. B **39**, 7744 (1989).

[2] H. M. Hill, A. F. Rigosi, K. T. Rim, G. W. Flynn, and T. F. Heinz, Nano Lett. **16**, 4831 (2016).

9:00am **2D+AS+NS+SS-ThM-4 Open-Source Controller for Scanning Probe Microscopy Applications***, M. Kangül, N. Asmari Saadabad, M. Penedo, **Georg Fantner**,* École Polytechnique Fédéral de Lausanne, Switzerland

Transferring the outcomes of academic research into patented industrial products converts the conceptual proof into accessible and sustainable technology. However, it is not always beneficial for researchers; as scientific studies often push the limits of instruments, requiring custom functionalities. In order to resolve these needs, several options are available, among which, hacking off-the-shelf products or rebuilding a simple copy of the existing technology are the most common ones. Either of these solutions slows down the research in a multidisciplinary field like Scanning Probing Microscopy (SPM). To not be limited by the disadvantages of the aforementioned solutions, we have developed an open-source SPM controller as a technology that eases innovation in not only our research but also in the whole SPM community.

In this regard, we have chosen a modular design strategy. A commercial FPGA (NI-7856R) with embedded real-time controller code sits at the core of the controller hardware. An FPGA adapter board for the flexibility of choosing different FPGAs, interconnect boards to perform digitally controlled (SPI) analog signal conditioning, such as filters and gain-offset stages, and a microscope adapter board to easily customize the input/output terminals of the controller for various SPM instruments are the other components of the modular hardware design. To run the controller, a custom software suite was developed in the graphical programming language LabVIEW (National Instruments). Similar to hardware, the software is also implemented in a highly modular fashion. The functions have been formulated into separate modules with minimum cross-dependency to reduce the complexity of coding for new developers.

The interest of our scientific and industrial collaborators in adapting and using our SPM controller in their instruments has motivated us to put an extra effort into building supporting documentation and creating an open-source platform. For the hardware, the documentation comprises design files, manufacturing guides, and assembly notes. For the software, documentation explaining the functionality of the real-time controller is provided, while the user interface side of the software is documented with user guides.

Here we report an open-source modular SPM controller provided with detailed documentation on both hardware and software levels. Modularity and documentation make it an easy-to-adapt instrument for various SPM applications. This platform has already been successfully adapted to control different SPMs such as contact mode AFM, AM-AFM, high-speed off-resonance tapping mode AFM, scanning ion conductance microscope, correlative AFM/SEM, and STM.

9:20am **2D+AS+NS+SS-ThM-5 Activation of Resistive Switching in TaOx on the Nanoscale***, **Olha Popova**,* ORNL

In present work we have shown two an alternative pathways to induce resistive switching of prototypical TaOx –(1) via direct biasing with a nanoscale AFM probe in oxygen free environment and (2) via He-ion patterning. Both approaches were carried out with fine control over the net amount of dissipated energy during activation. With direct AFM probe activation in oxygen free environment, we were able to switch conducting properties of the material in poorly controlled conditions. This is a similar pathway to electroforming, albeit combined with microscopy, which revealed directly the changes induced in the film during field-induced insulator-metal transition. Filamentary regions down to 20 nm in dimension could be routinely achieved by reducing the peak current during the activation cycle. Nevertheless, the process remains extremely stochastic. In contrast, by use of He ion irradiation pristine insulating state can be easily converted to conducting and resistively switching state without any breakdown, but the transition itself is a smooth function of ion-irradiation dose. These findings revealed numerous intermediate states of TaOx can be created by controlled ion-irradiation. Remarkably, this effect is directly compatible with device architectures, potentially allowing for a high-degree of on-demand tunning of neuromorphic circuitry and materials. By combining AFM and SEM-CL we were able to determine dependence of the ion dose/materials damage correlated with the chemical, structural and compositional tunability of thin TaOx films which offers significant opportunities to neuromorphic nanoelectronic materials in comparison with more mature technologies based on traditional bulk electronic materials.

9:40am **2D+AS+NS+SS-ThM-6 Probing Sub-Nanoscale Photophysical and Photochemical Processes via Localized Surface Plasmons: Vibrational Nano-Spectroscopy*, Sayantan Mahapatra,*** *N. Jiang,* University of Illinois - Chicago

Conventional spectroscopic techniques are limited by the optical diffraction limit to about half wavelength and therefore offer about 200 nm x 200 nm microscopic zone for working in the visible light range. Tip-enhanced Raman spectroscopy (TERS) emerges as an advanced analytical technique, where the plasmonically active probe is not only used to detect the tunneling current but also to interrogate the local chemical environment of the surface adsorbed molecules with angstrom scale precision. In this work, we report a topological and chemical analysis of two regioisomers (positional isomers), trans- and cis-tetrakispentafluorophenylporphodilactone (trans- and cis-H_2F_{20}TPPDL) by scanning tunneling microscopy (STM), ultrahigh vacuum (UHV) TERS on Ag(100) with the spatial resolution down to 8 Å, which has a wide range of applications in various field of surface science & nanotechnology such as regioselective catalysis reaction, chemical reactions, molecular electronics, etc. We have shown that it is possible to distinguish these two structurally very similar forms with high accuracy & precision. The two-component molecular junction has been identified using high resolution two-dimensional (2D) Raman mapping. Furthermore, the nanoscale molecule-substrate interactions have been addressed at the single-molecule level by employing different single-crystals i.e., Ag(100), Cu(100), and Au(100). Strong surface interactions at Cu(100) surface converted the flexible porphodilactone structure inverted, which was further verified by STM. In another case, the chemical transformation of adsorbed ferrocene dicarboxylic acid molecule was also analyzed via TERS on Cu(100) due to significantly strong interaction. Apart from the Raman signal enhancement, the highly energetic localized surface plasmons generated at the tip apex were utilized for site-selective C—Si bond activation inside a single 5,10,15,20-(tetra-trimethylsilylethynyl)porphyrin molecule. The nano-confined plasmonic field dissociated only one chemical bond, in presence of multiple chemically equivalent bonds inside the single molecule. To this end, multiple sites were also activated one by one and different types of products were visualized which could prove extremely useful in plasmon-induced site-selective heterogeneous catalysis application.

11:00am **2D+AS+NS+SS-ThM-10 Visualize Emergent Electron Orders in Two-Dimensional Quantum Materials*, Xiaomeng Liu,*** Princeton University **INVITED**

Recent developments have enabled scientists to isolate various 2D materials and assemble them into van der Waals heterostructures with elaborate stacking and alignments. These van der Waals materials, constructed layer-by-layer, host numerous novel quantum phases. However, most studies so far are done by electrical transport measurements, lacking spatial and energy resolution. Scanning tunneling microscopes (STM) can provide unique insights to these emergent quantum phases by visualizing the electron wave function in real space. Using our recent study of the graphene quantum Hall system as an example, I will demonstrate using STM techniques to identify broken symmetries, visualize electron wavefunctions, and imaging quasiparticles.

11:40am **2D+AS+NS+SS-ThM-12 Reconstruct the Intrinsic Force Landscape of Interfacial Interaction with Excitation-Enhanced Force Spectroscopy*, Alan Liu,*** *T. Sulchek,* Georgia Institute of Technology

The advancement of sensitive force transducers has enabled scientists to measure the subtle forces of interactions between molecules and interfaces at nanometer scales. Force spectroscopy techniques, such as dynamic force spectroscopy (DFS), extract a single representative force from each measurement, and require thousands of measurements with model assumptions to extract useful physical parameters of the interaction. This process is not only time consuming, but also the preciseness of the results relies largely on model assumptions, which make the results highly variable and dependent on experimental conditions. Furthermore, because DFS models presume the interaction to be a reversible reaction under certain energy/force landscape, parameters extracted by DFS method can only represent the rough shape of interaction landscape but not able to probe the detail landscape of underlying intrinsic interactions. Using our recently developed force spectroscopy framework[1], we can obtain the definitive intrinsic force landscape using a high sampling rate (above 1 MHz) atomic force microscopy (AFM) measurement. While most studies deemed the “snap” of AFM force measurement as an instantaneous action, we successfully sampled the fluctuation and real-time movement of the AFM probe at snap under a high sampling rate. At the snap location of each AFM force-distance measurement, transition points can be identified that define the bound state (or probe-in-contact state) and unbound state (or free oscillation state). Sampling at these transition points are key to probe the normally inaccessible portion of force landscape where the intrinsic force landscape has higher force gradient than the stiffness of the force probe. Next, we demonstrated how to modulate the snap locations of the force-distance curves by tuning the bandwidth of the excitation applied to the AFM probe. Lastly, we integrated the definitive forces sampled at various locations to reconstruct the intrinsic force landscape of the interaction without any model assumption or curve fitting process.

[1] Alan Y. Liu and Todd A. Sulchek, Reconstructing the Intrinsic Potential Energy Landscape of Interfacial Interactions with Thermally Modulated Force Spectroscopy, Phys. Rev. Res. 3, (2021).

12:00pm **2D+AS+NS+SS-ThM-13 AVS Graduate Research Awardee Talk: True Atomic-Resolution Imaging under Ambient Conditions via Conductive Atomic Force Microscopy*, Saima Sumaiya*[1]*,*** *M. Baykara,* University of California, Merced

Atomic-scale characteristics of surfaces dictate not only the governing principles of numerous scientific phenomena ranging from catalysis to friction, but also the design and performance of billions of state-of-the art nanoscale devices ubiquitous in modern life. Despite such an enormous significance, our ability to visualize surfaces on the atomic scale is severely limited by the strict conditions under which the related methods are operated. In particular, the two prominent methods utilized to achieve atomic-resolution imaging – scanning tunneling microscopy (STM) and noncontact atomic force microscopy (NC-AFM) – are typically performed under ultrahigh vacuum (UHV) and often at low temperatures. Perhaps more importantly, results obtained under such well-controlled, clean environments bear little relevance for the great majority of processes and applications that often occur under ambient conditions. Therefore, a method which is able to reliably and robustly image surfaces with atomic-level spatial resolution under ambient conditions can be regarded as a “holy grail” of surface science. Here, we first show that the method of conductive atomic force microscopy (C-AFM) can be utilized to achieve true atomic-resolution imaging under ambient conditions by imaging single atomic vacancies on molybdenum disulfide (MoS_2), without any control over the operational environment or elaborate sample preparation. With our method, we are also able to image several other types of defects on MoS_2, demonstrating that C-AFM can be utilized to investigate surface defects in a reliable, straightforward fashion under ambient conditions, in contrast to the often extensive operational requirements of STM and NC-AFM. We further employ the method of C-AFM to record atomic-resolution images on different classes of materials such as gold (metal), WSe_2 (semiconductor), $PtSe_2$ (semimetal), and α-Mo_2C (metallic transition metal carbide), proving its versatility in terms of the material classes it can be applied to. Our approach overcomes many of the classical limitations associated with STM and NC-AFM, and the findings herald the emergence of C-AFM as a powerful tool for atomic-resolution imaging under ambient conditions.

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[1] **AVS Graduate Research Awardee**

Actinides and Rare Earths Focus Topic
Room 318 - Session AC+AS+LS-ThM

Emerging Topics and Methods in Actinide/Rare Earth Science

Moderators: David Shuh, Lawrence Berkeley National Laboratory, **Alison Pugmire**, LANL, **Paul Roussel**, AWE, UK

8:00am **AC+AS+LS-ThM-1 Nuclear Forensics 2020:A Strategic Inflection Point*, David Willingham,*** Lawrence Livermore Laboratory **INVITED**

The terrorist attacks of 9/11/01 greatly increased the visibility of nuclear forensics, as policy makers became increasingly concerned about the possibility of well-organized terrorist groups obtaining a nuclear weapon or dirty bomb.The Departments of Defense (DOD), Energy (DOE), Homeland Security (DHS), and State (DOS), as well as the Federal Bureau of Investigation (FBI) and the intelligence community, all play key roles in nuclear forensics. DHS, for example, was founded in November 2002 and included, from the start, a formal nuclear forensics program in its Science & Technology Branch.An August 2007 presidential decision directive established the specific roles these agencies would play and formally established the National Technical Nuclear Forensics Center (NTNFC) within DHS to coordinate planning, integration, assessment, and stewardship of the U.S. government's nuclear forensics capabilities. In 2010, the Nuclear Forensics & Attribution Act established a National Nuclear Forensics Expertise Development Program (NNFEDP) within the NTNFC aimed at “developing and maintaining a vibrant and enduring academic pathway from undergraduate to post-doctorate study in nuclear and geochemical science specialties directly relevant to technical nuclear forensics.”National laboratories like LLNL have particularly benefitted from the establishment of postdoctoral fellowships.

In 2021, primary responsibility for nuclear forensics within the US Government transferred from DHS to the National Nuclear Security Administration (NNSA) within DOE with the issuance of National Security Presidential Memorandum 35, National Technical Nuclear Forensics. However, the Nuclear Forensics & Attribution Act of 2007 is still in force, which defines certain roles for DHS, particularly for stewardship of the nuclear forensics’ workforce. Starting with the FY21 budget, there have been substantial increases in funding for NNSA for both nuclear forensic operations and R&D. However, the exact configuration of the nuclear forensics expertise development program(s) going forward is still being determined.”

This talk will highlight some of the outstanding research conducted by our DHS postdoctoral fellows, including:

- Development of RIMS as a tool for in situ analyses for nuclear forensics.
- Improved determination of half-lives and branching ratios important for U rad-chem
- Exploration of the use of isochrons for age dating of impure samples.
- Development of new stable isotopic systems as new sources of signatures for nuclear forensics.
- Development of rapid methods for dissolving solid samples

8:40am **AC+AS+LS-ThM-3 The Non-Integer Occupancy Ground State Hypothesis*, Miles Beaux,*** Los Alamos National Laboratory **INVITED**

A deeply ingrained and long-standing practice exists for identifying integer orbital occupancy ground state electronic configurations for neutral atoms of the elements. For certain elements, the identification of the electron occupancies of the orbitals in a neutral atom can be a controversial topic, instigating heated debate among scientists. The pedagogy of how atomic structure and the periodic table are initially taught might serve as a driver for this practice. For example, the octet rule is often used to explain the most energetically favorable ionic states, similarities in properties of like-group elements, and the most stable compounds formed by the transfer and sharing of electrons. However, the octet rule is also insufficient to explain the existence, structure, and properties of transition metal elements, including the lanthanides and actinides.

A more fundamental quantum-based understanding of electronic structure provides a firm basis for the overall structure of the periodic table. Specifically, the octet rule is understood as the stability of completely filled *s*-, and *p*-orbitals each having electron capacities of two (l=0; m_l=0; m_s=±½) and six (l=1; m_l=-1,0,+1; m_s=±½), respectively, with each Period, *n*, having n_s and n_p orbitals (except for Period 1, for which no 1*p* orbital exists). Extrapolation of this quantum mechanical underpinning of the Periodic Table explains the existence of the *d*- and *f*-blocks. The filling patterns of the orbitals for elements in the Period Table reveals relative energies of the various orbitals. Deviations from the filling pattern are often explained to varying degrees of satisfaction by the interplay between Hund’s rule and the Aufbau principle for near-degenerate states; the stability of empty, half-filled, and completely filled orbitals; and core level screening. As the energy landscape for electron orbitals becomes more crowded for higher Period elements, the potential for near energy degenerate states increases. The potential for quantum superposition of electrons in these near energy states leading to effective non-integer orbital occupancies will be discussed in the context of observed instabilities in actinide and rare earth elements. Experimental and theoretical efforts to investigate this hypothesis for a series of Np, Pu, and Am compounds will also be described.

9:20am **AC+AS+LS-ThM-5 Legacy Plutonium at the Hanford Site*, Edgar Buck*, *D. Reilly, G. Hall, K. Kruska, L. Liu, S. Triphathi, B. McNamara, A. Casella, D. Meier,* Pacific Northwest National Laboratory **INVITED**

The morphological characteristics of plutonium materials may provide information on the processes that were used to create the material; however, understanding of the detailed thermodynamic and kinetic processes needed to predict the evolution of its particle size distribution, crystal habit, and agglomerated state is still evolving. There has been an effort to fill this technical gap using an integrated experimental and modeling approach for formation of plutonium phases, including oxides and oxalates. Several different types of plutonium phases have been observed in wastes at the Hanford site, such as the Z9 crib near the former plutonium finishing plant and plutonium solids found in the SY102 and TX118 tanks. Laboratory experiments have been conducted to probe the formation mechanisms for these materials. By examining the preciptiating plutonium solids using a combination of in-situ optical microscopy (OM), scanning electron microscopy (SEM), cryo-electron microscopy (CryoEM) and in-situ transmission electron microscopy (TEM)., we have been able to demonstrate the occurrence of non-classical crystalline pathways for plutonium particle growth in some instances.

Understanding crystallization pathways in plutonium materials depends on the ability to unravel relationships between the intermediates and final crystalline products at the nanoscale, which is a particular challenge with radioactive materials. However, these powerful new tools of in-situ and cryoEM are providing new insights into the plutonium chemical system. The experimental data is helping to parameterize the computational modeling with the potential to lead to the development of predictive tools for identification.

11:00am **AC+AS+LS-ThM-10 Focused Ion Beam for Spatially Resolved Morphological Analysis of Nuclear Materials*, Brandon Chung*,** *S. Donald , D. Rosas, S. Sen-Britain, V. Som, N. Teslich, A. Baker,* Lawrence Livermore National Laboratory*; A. Ditter, D. Shuh,* Lawrence Berkeley National Laboratory

Nuclear forensics requires accurate identification of distinguishing material characteristics of interdicted nuclear materials. Local morphological and chemical variations in nuclear materials are nearly ubiquitous due to the varying provenance, process, and pathways. Conventional analysis using bulk nuclear material provides an overall analytical value, but a typical nuclear material is heterogeneous, requiring highly spatially resolved characterization. Consequently, averaging material characteristics may obscure critical forensic signatures resulting from local chemical and structural variations. We will describe our efforts to strengthen operational and scientific methodologies to employ the focused ion beam-scanning electron microscopy (FIB-SEM) on uranium (U) and plutonium (Pu) materials for direct three-dimensional (3D) morphological analysis or to prepare site-specific material features to obtain spatially resolved characterizations using transmission electron microscopy (TEM) and X-ray synchrotron spectromicroscopy. Our work shows the internal morphological and chemical variations in host nuclear materials provide valuable information about the material’s production processes and recent environmental exposures. We identified that internal microscopic features entrapped within bulk nuclear materials contain trace elements or chemical that are attributable to their origin, processing, and environmental exposures.

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Security Administration. This support does not constitute an express or implied endorsement on the part of the Government. LLNL-ABS-835643

11:20am **AC+AS+LS-ThM-11 Studying Combined Influence of Alpha Irradiation and Dissolved Hydrogen on UO_{-2} Corrosion Using a Microfluidic Electrochemical Cell**, ***Jennifer Yao***, *B. McNamara, M. O'Hara,* Pacific Northwest National Laboratory; *N. Lahiri,* Pacific Northwest National Lab; *E. Ilton, C. Wang, E. Buck,* Pacific Northwest National Laboratory

It is well accepted concept that α-decay is the most important source of radiation in the spent nuclear fuel (SNF) after 1,000 years ^{1}. The influence of α-irradiation in the presence of dissolved H_2 on the corrosion of UO_2 can provide important information to assess the impact of the long-term SNF to the storage environment. However, experiments with bulk amount of SNF are expensive owing to the need for shielded hot cell facilities to protect researchers from the intense radiation field. To address this challenge, we employed a novel invention, particle-attached microfluidic electrochemical cell (PAMEC), to investigate UO_2 corrosion under different conditions (e.g., α-irradiation and H_2) at the microscale. Less than 10 μg of UO_2 (containing 1% to 10% $^{233}UO_2$) powder was mixed with polyvinylidene fluoride (PVDF) and carbon black to form the working electrode and included into PAMEC, which ^{233}U was used as alpha source to simulate the"aged" spent fuel ^{2}. The response of the corrosion potential of a ^{233}U contained UO_2 working electrode to dissolved H_2 in 0.1 M $NaClO_4$ (pH=9.5) will be presented. In addition, the 50nm thick Si_3N_4 detection window on PAMEC allows in situ imaging of the corrosion process using the high-resolution imaging technique, such as scanning electron microscope (SEM) coupled withEnergy-dispersive X-ray spectroscopy (EDS). Furthermore, X-ray photoelectron spectroscopy (XPS) was used to determine the oxidation state of the UO_2 electrode that was exposed to alpha radiation and dissolved H_2. Our work demonstrates the study of combined influences on UO_2 corrosion under the conditions that are known to be present in the long-term SNF environment by employing a microfluidic electrochemical cell. We vision this approach can be widely applied to study the influences of conditions that resemble the practical repository environment on SNF, while with greatly reduced hazardous risk when performing such experiments.

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11:40am **AC+AS+LS-ThM-12 A Model to Extract the Size-Dependent Surface Structure of Actinide Oxide Nanoparticles**, ***Shinhyo Bang***, *L. Moreau,* Washington State University

Characterization of actinide oxides at the nanoscale presents unique challenges due to their radioactivity, high surface area, and inherent diffraction broadening due to small grain size. Extended x-ray absorption spectroscopy (EXAFS) is an analytical method to investigate atomic-scale structural properties that enables their encapsulation and does not rely on long-range order. There is a limitation that EXAFS only gives the averaged structural information of heterogeneous samples. We aimed to deconvolute EXAFS results to extract the surface coordination environment of UO_2 NPs by proper modeling, and investigate how it evolves with varying sizes (1.4, 4.7, 8 nm). The termination effect was used to quantify the surface terminating species of UO_2 NPs. A higher degree of oxygenation on the surface was observed for 8 nm NPs. EXAFS simulation was implemented to backtrack the surface structure of these NPs. It was observed that the bond contraction due to the surface relaxation effect was localized in a few outermost layers of NPs and the surface disorder of 1.4 and 4.7 nm NPs was significantly enhanced from that of bulk.

Applied Surface Science Division
Room 320 - Session AS+AC+BI+CA+HI-ThM

Unraveling the Composition of Complex Systems with SIMS

Moderators: Steve Consiglio, Tokyo Electron, **Gregory L. Fisher**, Physical Electronics

8:20am **AS+AC+BI+CA+HI-ThM-2 Ex-Situ, Surface and Bulk Investigations of Defluxing Chemistry Effects on Solder Mask**, ***J. Elliott Fowler,*** Sandia National Laboratories; *R. Gerhardt,* Georgia Institute of Technology; *J. Ohlhausen, R. Callaway,* Sandia National Laboratories; *M. Watt,* Georgia Institute of Technology; *S. Grosso, S. Rosenberg,* Sandia National Laboratories

Solder masking is an integral process in the manufacture of printed circuit board assemblies (PCBAs) – it serves to protect the unfinished copper traces from environmental effects, define the soldering pads and provide an adherable surface for conformal coating. Liquid photo-imageable (LPI) solder mask is one of the most popular choices for PCBAs due to ideal electrical and physical properties as well as chemical. LPI solder mask is a heterogeneous epoxy acrylate-based matrix, thus its surface chemistry can be very distinct from its overall bulk chemistry. The surface chemistry is of particular interest as it must be compatible with and resistant to a wide range of chemistries and environments which the PCBA will experience during its production and fielding lifetime. For instance, sensitivity to moisture is a well-known issue. Several studies of solder mask moisture absorption reveal that it reaches a saturation of ~1 weight percent in high-humidity environments, and corresponding changes in insulative properties occur. Risks to mask performance have arisen as a result of the use of new flux formulations which require increasingly aggressive aqueous defluxing chemistries for removal. We hypothesize that alkaline defluxing chemistries will significantly modify the surface chemistry of solder mask, making it more vulnerable to moisture and thus deteriorating their insulative properties.

A commercially available LPI solder mask material was prepared on squares of FR4 board and exposed to increasingly alklaine cleaning chemistries: including DI water, a pH neutral and a pH >10 defluxing chemistry. Samples were tested with three complementary surface-sensitive analytical techniques, x-ray photoelectron spectroscopy (XPS), time of flight secondary ion mass spectrometry (TOF-SIMS) and contact angle goniometry. TOF-SIMS results show that both pH neutral and alkaline chemistries alter the surface, removing PDMS and leaving organic residues. Contact angle goniometry shows that the alkaline chemistry makes the board's surface significantly more hydrophilic. XPS results show a decrease in Si at the surface correlating to a decrease in PDMS versus the control, with the largest decrease occurring due to the alkaline chemistry. In all cases, the surface is somewhat recoverable; however, recovery is less pronounced with increasing pH. AC impedance spectroscopy and DC Surface Insulation Resistance (SIR) testing of exposed samples in elevated humidity environments was performed to resolve changes in insulative performance due to observed changes in mask surface chemistry.

SNL is managed and operated by NTESS under DOE NNSA contract DE-NA0003525

8:40am **AS+AC+BI+CA+HI-ThM-3 Unraveling the Composition of Complex Systems with SIMS**, ***Birgit Hagenhoff,*** Tascon GmbH, Germany **INVITED**

For more than four decades SIMS has proven to be a valuable tool in academic research as well as for industrial applications. Whereas the first years focussed on understanding the underlying physical processes using mono-elemental samples, the advent of ToF-SIMS (Time-of-Fligt Secondary Ion Mass Spectrometry) instrumentation in the 80s of the last century opened the path to using SIMS as a screening tool for characterising "the unknown", i.e. samples about which hardly anything is known before the analysis, where sample preparation should be as scarce as possible and where the analysis is performed without any chromatographic pre-step to separate out sample compounds.

Over the years, intensive discussions between those developing instruments and those applying them on a daily basis lead to a fruitful and steep learning curve in the SIMS communities. Meanwhile SIMS instruments offer a multitude of operational modes and are capable of analysing as 3D volume pixel by pixel. The lateral resolution has almost reached the physical limit of the collision cascade with values well below 100 nm and a depth resolution in the nm-range can be achieved. The development of cluster ion sources leads to the possibility to also probe organic materials in depth. At the same time data evaluation routines have become more powerful to address the large amount of data (several GByte for a 3D data set).

Generally, users would like to address three main questions: what (identification) is sitting where (localization) and how much is it (quantification)? Whereas the localization problem, as mentioned above, meanwhile is comparatively straightforward, identification and quantification still are challenging. In identification, the parallel presence of many elements and organic compounds in the SIMS spectra still asks for an expert to solve the analytical puzzle. Here, the application of multivariate statistical techniques and, more recently, machine learning approaching offer promising paths into the future. For a reliable quantification, the influence of the SIMS matrix effect on the results has to be taken into account. Here, the availability of suited reference samples plays a key role for closing the gap to quantitative techniques, like e.g. XPS (X-ray Photoelectron Spectroscopy).

The talk will therefore focus on identification and quantification issues including the use of multivariate statistics, MS/MS approaches and the use of reference sample comparing SIMS with the quantitative techniques XPS and LEIS (Low Energy Ion Scattering).

9:20am **AS+AC+BI+CA+HI-ThM-5 Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS) as a Novel Approach to the Characterization of Coatings and Interfaces of Porous Transport Layers***, **Genevieve Stelmacovich**, M. Walker, J. Foster,* Colorado School of Mines*; D. Cullen ,* Oak Ridge National Laboratory*; A. Paxson ,* Plug Power*; G. Bender, T. Schuler, S. Ware,* National Renewable Energy Laboratory*; S. Pylypenko,* Colorado School of Mines

The United States energy infrastructure aims to move towards the integration of hydrogen energy. As such, the production of reliable hydrogen generation through the optimization of water electrolyzers is imperative. In proton exchange membrane water electrolyzes (PEMWE's), the porous transport layer (PTL) plays an important role. Due to the harsh conditions of the cell, titanium is the current state-of-the-art anode PTL material. However, titanium quickly forms a layer of titanium oxide which significantly decreases conductivity of the PTL and respectively decreases the overall efficiency of the PEMWE system. To mitigate oxide effects, coatings are commonly applied to the PTL.

Focused Ion Beam Scanning Electron Microscopy (FIB-SEM) in conjunction with Scanning Transmission Electron MicroscopyEnergy-dispersive X-ray Spectroscopy (STEM-EDS) analysis is a commonly used technique to characterize PTL materials and PTL coatings, specifically to look at coating homogeneity and unfavorable oxide layer formation. Unfortunately, this approach is both time-consuming and labor intensive. Additionally, STEM-EDS analysis only provides elemental information, so if several oxide layers preside, it can be difficult to differentiate them, and thus lead to a lack of understanding fundamental degradation mechanisms. These technique deficiencies have motivated the development of an alternative approach that allow more efficient characterization of these materials. Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) is a valuable technique that is commonly used to characterize thin films and buried interfaces. ToF-SIMS can be performed relatively quickly, provides chemical information, and is sensitive to trace elements. This technique also enables visualization of elemental distribution, which provides more detailed surface and interface information. This presentation will demonstrate capabilities of ToF-SIMS for characterization of PTLs comparing results to TEM analysis of cross-sections obtained with FIB-SEM. This study will highlight similarities and differences between the techniques, expand on technique optimization for these morphologically challenging samples, and suggest paths for future investigation moving forward.

9:40am **AS+AC+BI+CA+HI-ThM-6 Construction of Accurate 3D NanoSIMS Depth Profiling Images of Cells in the Presence of Lateral Variations in Sputter Rate***, M. Brunet, B. Gorman, **Mary Kraft**,* University of Illinois Urbana-Champaign

We have developed a strategy for constructing accurate 3D NanoSIMSdepth profiling images of cells in the presence of lateral variations in sputter rate. In this strategy, we use the secondary electrons acquired in parallel with the negative ions during depth profiling to reconstruct the 3D morphology of the cell every time a depth profiling image is acquired. The morphologies created for each raster plane in the depth profile are adjusted to ensure that the height at every pixel decreases with increasing image plane. The resulting reconstructions of the cell's morphology are used to define the z-positions of the voxels in the component-specific 3D NanoSIMS images. We validated this strategy by comparing morphology reconstructions for secondary electron depth profiling images acquired with focused ion beam - secondary electron microscopyand AFMdata acquired from the cell before depth profiling. The shape, curvature, and relative height of the reconstructed morphology agreed well with the AFM data. Depth correction of 3D NanoSIMSdepth profiling data of a metabolically labeled mammalian cell using this strategy improved visualization of the^{18}O-cholesterol and ^{15}N-sphingolipids distributions intransport vesicles and organelle membranes. Accurate 3D NanoSIMS images that show the intracellular distributions of molecules of interest may now be constructed in the presence of variations in sputter rate and the absence of correlated topography data.

11:00am **AS+AC+BI+CA+HI-ThM-10 Innovations in Nuclear Materials Analysis with SIMS***, **Christopher Szakal**,* National Institute of Standards and Technology (NIST) **INVITED**

Global nuclear safeguards efforts, coordinated by the International Atomic Energy Agency (IAEA), require precision measurements to answer questions related to nuclear treaty compliance. Despite those questions seeming relatively simple, and the elemental composition of the target analytes often consisting of just uranium and oxygen, the complex processes employed to answer those questions reveal the importance of subtle nuances to meet analytical objectives. This presentation will explore the complexity of this type of analyte system and how innovations in secondary ion mass spectrometry (SIMS) resulted in a routinely utilized tool to address nuclear safeguards requirements for environmental sampling analysis. The complexity is largely driven by the small amounts of nuclear particle material available for analysis, including challenges for 1) representative sampling of analyte material to represent actual nuclear processes, 2) accuracy and precision of uranium isotopic analyses across a wide dynamic range, and 3) determining when a nuclear process created the analyte material. Precision SIMS measurements provide the opportunity to address these analytical complexities to answer key nuclear safeguards questions, but the presentation will also highlight when limitations are inevitable for which questions can be answered.

11:40am **AS+AC+BI+CA+HI-ThM-12 Understanding Surface Bonding and Molecular Structure with MS/MS Imaging: From Click-Chemistry to Biogenesis***, **Gregory L. Fisher**,* Physical Electronics

A TOF-TOF imaging mass spectrometer allows TOF-SIMS (MS^1) imaging and tandem MS (MS^2) imaging to be achieved in a lossless fashion [1,2]. Secondary ions for MS^1 and MS^2 analysis are produced from the same surface area by a primary ion nanoprobe. Monolayer film samples may be characterized without undesired erosion or degradation; even sub-monolayer 2D films are readily characterized. Kilo-electron volt collision-induced dissociation (keV-CID) enables compositional identification and structural elucidation of precursor ion moieties. This analytical capability has been brought to bear for straightforward molecular identification as well as multifaceted studies involving surface modification, polymers, composites, catalysis, forensic and failure analysis, biology and pharmaceuticals. TOF-SIMS tandem MS imaging was employed to unravel the click-chemistry of sub-monolayer films [3] and shed new light to unlock the mystery of molecular biogenesis [4,5].

References

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[3] S. Oh, et al, *Chem. Mater*. **32** (2020) 8512-8521.

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12:00pm **AS+AC+BI+CA+HI-ThM-13 Probing Grain Boundary Segregation in 304L Stainless Steel using Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS)***, **James Ohlhausen**, E. Barrick, D. Susan, C. Robino, K. Hattar, J. Herrmann, P. Duran, J. Rodelas,* Sandia National Laboratories

Boron-rich phases in austenitic stainless steels can promote liquation cracking in the heat affected zone during welding. Stainless steels with boron concentrations even as low as 20 wt. ppm are susceptible to grain boundary cracking after heat treatments. The kinetics of phase transformations during heat treatment that generate the crack susceptible microstructure are currently unknown. Time-of-flight Secondary Ion Mass Spectrometry (ToF-SIMS) was used to map Boron at grain boundaries and in the bulk at trace levels for a series of 304L stainless steel coupons that were heat treated across a range of temperatures and cooling rates to investigate these phase transformations.ToF-SIMS and Scanning electron microscopy (SEM) were used to observe the distribution of chromium borides before and after heat treatment. These results will be used to enable quantitative prediction of thermal processing conditions to avoid weld cracking.Sample preparation methods, ToF-SIMS acquisition conditions and data analysis will be discussed.

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Electronic Materials and Photonics Division
Room 304 - Session EM+AS-ThM

Photovoltaic Materials, Characterization, and Applications

Moderator: Seth King, University of Wisconsin - La Crosse

11:00am **EM+AS-ThM-10 Translating Materials-Level Characterization of Carbon-Nanotube-Reinforced Composite Gridlines To Module-Level Degradation***, **Sang Han,*** The Univeristy of New Mexico and Osazda Energy*; A. Chavez,* The University of New Mexico and Osazda Energy*; B. Rummel,* The University of New Mexico and Osazda Energy*; A. Jeffries,* Osazda Energy*; N. Bosco,* National Renewable Energy Laboratory*; B. Rounsaville , A. Rohatgi,* Georgia Institute of Technology

Cell cracks in PV modules caused by environmental stressors and extreme weather events can lead to gradual or immediate power degradation. To directly address cell-crack-induced degradation, we have formulated a carbon nanotube additive for commercial silver pastes used in screen printing. We have shown in earlier work that these metal matrix composites do not impact the cell efficiency, while enhancing the metallization's fracture toughness and electrical gap-bridging capability. In this work, we focus on translating materials-level characterization techniques to module-level degradation. We found that we get conflicting results from two different materials characterization methods of measuring the metallization's ability to electrically bridge gaps in cracked solar cells. To determine which materials characterization method correlates better with the mini-module degradation characteristics, we have conducted stress testing for a small dataset of mini-modules.

The first characterization method for measuring the metallization's ability to electrically bridge cell cracks is dubbed as Resistance Across Cleaves and cracKs (RACK), in which a piezoelectric stage pulls apart fractured cells in submicron increments while the resistance of the gridlines on top of the fractured cells is measured until the gridlines electrically fail. The tensile stress applied to the metallization during the RACK test is intended to mimic the stress encountered by the metal gridlines during thermal cycling after cell fracture, in which cell fragments translocate within the module. Another common method for characterizing the metallization's ability to electrically bridge cell cracks is three-point bending test, where a rectangular substrate with two parallel gridlines, laser-diced from a cell, is mounted on an acrylic beam and placed in a three-point bend fixture while the resistance of gridlines is monitored as a crack in the cell is slowly opened. The failure mechanism with this testing method could be an alternative representation of how a cell would fracture when the module is being flexed under heavy mechanical loads or being stepped on.

The two materials-level characterization methods described above are designed to measure the metallization's ability to electrically bridge a cracked cell; however, they give conflicting results as to which composition and geometry of carbon nanotubes performs best. To better understand which materials-level test correlates to module-level degradation, 2x2 minimodules were constructed with pre-fractured cells and subjected to thermal cycling.

11:20am **EM+AS-ThM-11 Effects of Carbon-Nanotube-Reinforced Composite Gridlines on Photovoltaic PERC Cell and Module Efficiency***, **Andre Chavez,*** The University of New Mexico and Osazda Energy*; S. Han,* The Univeristy of New Mexico and Osada Energy*; A. Jeffries,* Osazda Energy*; S. Huneycutt,* The Univeristy of North Carolina at Charlotte*; A. Ebong,* The University of North Caronlina at Charlotte*; D. Harwood, N. Azpiroz,* D2 Solar

Abstract — The addition of carbon nanotubes (CNTs) in commercial silver pastes used for the front metallization of Passivated Emitter and Rear Contact (PERC) solar cells not only helps improve the materials toughness and resilience to cell cracks, but also offers some improvement to cell efficiency. A large data set of 87 cells containing the CNT-enhanced metal matrix composite (MMC) gridlines, when compared to a set of 66 baseline PERC cells, shows an increased efficiency by 0.03%, which is the threshold that cell and module manufactures care about. Six mini-modules, each of which consists of two PERC cells connected in series, were fabricated with the baseline metallization, and six mini-modules were fabricated with MMC-enhanced PERC cells. Three modules were subjected to 200 cycles of thermal shock (TS) from -40 to +85 °C, and the remaining three were subjected to highly accelerated stress testing (HAST), where damp heat is applied at 120 °C for 100 hours and 100% relative humidity. After these two tests, the MMC metallization shows comparable corrosion to the baseline metallization and power loss of less than 0.6% after TS-200 and less than 4% after HAST-100. The inclusion of CNTs to conventional screen printable silver pastes has the ability to improve cell efficiency, while showing statistically identical beginning-of-life cell and module performance as well as corrosion characteristics and infant failure rate (e.g., solder bond failure) comparable to the baseline. These results show strong promise for commercial implementation of the MMC-enhanced metallization to improve PV module reliability.

This material is based upon work supported by the U.S. Department of Energy's Office of Energy Efficiency and Renewable Energy (EERE) under the Solar Energy Technologies Office Award Number DE-EE0009013.

11:40am **EM+AS-ThM-12 Atomic Layer Deposition of NiO for Single Junction Perovskite and Tandem Perovskite/Silicon Photovoltaics***, N. Phung, C. van Helvoirt,* Eindhoven University of Technology, The Netherlands*; D. Zhang, V. Zardetto, B. Geerligs,* TNO Science and Industry, the Netherlands*; M. Verheijen, E. Kessels, B. Macco,* ***Mariadriana Creatore,*** Eindhoven University of Technology, The Netherlands

Metal halide perovskite absorbers have attracted major attention due to their excellent opto-electronic properties. Recent advancements in performance and stability of perovskite solar cells (PSCs) have been achieved with the application of self-assembled monolayers (SAMs), serving as hole transport layers in the p-i-n PSC architecture [1]. However, a reproducible implementation of SAM in the PSC device requires knowledge of its surface coverage on ITO since non-covered areas in direct contact with perovskite may lead to shunts and low open-circuit voltage.

In this contribution, we investigate the influence of an atomic layer deposited (ALD) NiO film (7 nm) on the surface coverage of SAM for single junction PSC as well as tandem PSC/silicon devices. NiO is processed either by plasma-assisted ALD [2] or thermal ALD [3]. The latter has also been developed since thermal ALD is often adopted in upscalable technologies such as batch and spatial ALD.

We observe that the SAM of MeO-2PACz ([2-(3,6-dimethoxy-9H-carbazol-9-yl)ethyl]phosphonic acid) inhomogeneously covers ITO. Instead, when adopting NiO as intermediate layer between ITO and SAM, the SAM homogeneity and surface coverage improve, as witnessed by transmission electron microscopy (TEM) and conductive atomic force microscopy. This result is explained in terms of chemisorption reactions between SAM phosphonic acid groups and NiO hydroxyl groups. The SAM homogeneity on NiO leads to higher shunt resistance in the device with respect to the one with SAM directly processed on ITO. Moreover, the combination of NiO and SAM results in a narrower distribution of device performance reaching more than 20% efficient champion device.

The above-mentioned merits of ALD NiO are further exploited in a monolithic tandem device, consisting of a c-Si passivated emitter rear cell (PERC) bottom cell and a perovskite top cell. In the case of ITO/SAM tunnel junction, several devices present electrical shunts in the top cell, leading to a standard deviation of efficiency of 4.6% across device batches. In the case of ITO/NiO/SAM tunnel junction, the tandem device exhibits a narrow distribution of efficiency (standard deviation of 2% across device batches) because of the uniformity and conformality of NiO on ITO, as witnessed by TEM analysis. A champion efficiency of 23.7% is recorded, among the best tandem cell efficiency implementing an industrial standard bottom cell.

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12:00pm **EM+AS-ThM-13 XPS Depth Profiling of Single Film and Two-Layer Heterojunction Metal-Halide Perovskites***, **Jennifer Mann,*** Physical Electronics*; C. Clark, W. Hsu, E. Pettit,* University of Minnesota*; K. Artyushkova,* Physical Electronics*; R. Holmes,* University of Minnesota

The goal of an XPS depth profile is to obtain accurate identification of layer thicknesses and composition as a function of depth within film structures. Monatomic Ar^+ has been available for many years and is often the gun of choice for inorganic thin film profiling despite its issues with preferential sputtering, material migration, and chemical reduction that may occur, thus altering the apparent profile of the analyzed material.

The introduction of C_{60} cluster ion beam and argon gas cluster ion beam (GCIB) sputtering in recent years has expanded the types of materials that may be studied by depth profiling beyond that of inorganic thin films.Cluster type ion guns have shown successful depth profiling of polymer and organic materials as well as inorganic thin film structures while preserving the stoichiometry and chemical structures.

Organo-metal-halide perovskites are of interest due to their promising application in solar cells, where they have achieved efficiencies above 25%.In this work, we present XPS depth profiles of single films of metal-halide perovskites, with an ABX_3 structure(A = MA - methylammonium or Cs, B = Sn or Pb, X = Br or I).Maintaining stoichiometry while sputtering can be very challenging, so in addition, $MAPbI_3$ was analyzed with hard X-ray photoelectron spectroscopy (HAXPES). A Cr Kα (5414.8 eV) X-ray source provides information depths three times greater than the standard Al Kα (1486.6 eV) X-ray source.Using a higher energy photon provides a non-destructive method to probe deeper into the sample, minimizing the contribution from surface oxides and carbon contamination.

XPS depth profiles were obtained on a single layer perovskite film using the two cluster ion guns, available on the PHI *VersaProbe* III - C_{60} and argon gas cluster (GCIB) The viability of each gun in maintaining both the stoichiometry and chemistry of the film as it was sputtered was determined before measuring a more complex perovskite system.

A more complex two-layer heterojunction of organo-metal-halide perovskites was also investigated using optimized ion sputtering conditions.This is a particularly well-suited system for XPS depth profiling due to the accessible thicknesses of the layers and the significant difference in the chemistry of carbon and nitrogen in different organic A-site cation environments. Indeed, this difference is exploited to probe ion migration and mixing across perovskite interfaces.

Electronic Materials and Photonics Division
Room 304 - Session EM+MN+TF-ThM

Wide and Ultra Wide Band Gap Materials and Devices

Moderators: Erica Douglas, Sandia National Laboratories, **Rehan Kapadia**, University of Southern California, **Rachael Myers-Ward**, U.S. Naval Research Laboratory

8:00am **EM+MN+TF-ThM-1 What Can We Do With Ga_2O_3?*, Man Hoi Wong,*** University of Massachusetts Lowell **INVITED**

The past few decades have witnessed technological innovations driven by physical electronics solutions embodying novel materials and device concepts that fundamentally change our lives today. Ultrawide-bandgap semiconductors represent a new area of intensive research covering a wide spectrum of materials, physics, devices, and applications. As the critical electric field of avalanche breakdown increases super-linearly with increasing bandgap energy, ultrawide-bandgap semiconductors can address critical needs across many areas including energy-efficient power switching, radio-frequency power, and electronics in harsh thermal or radiation environments. I will illustrate efforts to pursue these visions with Gallium Oxide (Ga_2O_3) devices, which have been making rapid strides thanks to ongoing breakthroughs in crystal growth and device processing technologies. Demonstrations of multi-kilovolt breakdown, normally-off operation, vertical device concepts, and heterostructures have positioned Ga_2O_3 devices as relevant contenders for practical applications. In this talk, the achievements on various types of Ga_2O_3 power switches and rectifiers will be reviewed. Materials science pertinent to the implementation of those device concepts will be highlighted. Several approaches to address challenges related to field management and doping will be discussed, using our recent work on enhancement-mode Ga_2O_3 power transistors as an illustration. We are also developing a novel Ga_2O_3 ultrahigh-speed transistor concept that harnesses quasi-ballistic transport effects through heterojunction engineering to reduce carrier transit delay. Such a device can simultaneously serve as an effective spectroscopy tool for studying hot-carrier dynamics in Ga_2O_3. This as well as other types of Ga_2O_3 quantum devices have seen scant experimental and theoretical developments to date and represent a fertile ground for research.

8:40am **EM+MN+TF-ThM-3 Controlled Growth of Epitaxial Ga_2O_3 Polymorphs for Ultra-Wide Bandgap Semiconductor Devices*, Lisa Porter,*** *K. Jiang, J. Tang, M. Cabral, R. Davis,* Carnegie Mellon University, USA

Gallium oxide (Ga_2O_3) is attracting increased interest for electronics that can operate in extreme conditions, such as high power, high temperature and high radiation fluxes. This ultra-wide bandgap semiconductor has an interesting feature in that it exists in different phases, or polymorphs. β-Ga_2O_3 is thermodynamically stable at atmospheric conditions up to its melting point and is therefore the phase produced in melt-grown, single-crystal substrates.Epitaxial films of the other metastable polymorphs, however, are also of interest because they possess unique properties – such as high spontaneous polarization, ferroelectricity, or ferromagnetism – that could lead to new types of heterostructure devices.In this presentation we will summarize our results on the growth of epitaxial films of phase-pure vs. mixed-phase ε(κ), β, and γ-Ga_2O_3 using metal-organic chemical vapor deposition.We will focus on variables (temperature, triethylgallium (TEG) flow rate, and type of substrate) that have led to optimum control over the resulting polymorph and its microstructure, as characterized using x-ray diffraction (XRD), scanning electron microscopy, and high-resolution transmission electron microscopy (TEM).For example, for growth on (0001) sapphire substrates the phase composition of a 700-nm-thick epitaxial layer – from nominally 100% ε(κ) to 100% β-Ga_2O_3 – can be controlled by varying the substrate temperature (470 °C to 570 °C) and TEG flow rate (0.29 sccm to 2.1 sccm).We also show that nominally single-phase γ-Ga_2O_3 and β-Ga_2O_3 epitaxial films are produced under the same growth conditions (in the same growth run) by employing different substrates.High-resolution TEM and XRD ω-2θ and phi-scans suggest that the γ-Ga_2O_3 films are single crystal.

9:00am **EM+MN+TF-ThM-4 Plasma Enhanced-ALD Amorphous Gallium-Oxide Channel Thin Film Transistors for Back-End-of-Line Integration*, Charlotte Van Dijck,*** Helmholtz-Zentrum -Berlin für Materialen und Energy, Germany*; F. Maudet,* Helmholtz-Zentrum-Berlin für materialen und Energy, Germany*; S. Banerjee, V. Deshpande, C. Dubourdieu,* Helmholtz-Zentrum Berlin für Materialen und Energy, Germany

Amorphous metal oxide semiconductors exhibit promising properties such as high mobility at low deposition temperatures (< 400°C) and hence are widely investigated as channel materials for thin film transistors (TFT). The low processing temperature also enables their integration on the back-end-of-line (BEOL) of Si CMOS circuits for More-than-Moore applications. While amorphous Indium Gallium Zinc Oxide (IGZO) and Indium Zinc Oxide (IZO) are the most studied amorphous metal oxides for TFT applications, amorphous gallium oxide (a-GaO_x) is interesting due to its ultrawide bandgap (~4.9 eV) combined with the ability to control the carrier density by varying the oxygen content in it [1]. Thus, a-GaO_x has potential for high voltage TFT, sensing, and memristive device applications. There have been few reports of a-GaO_x TFTs with pulsed laser deposition or solution processing, yet a detailed study of TFTs featuring ALD based a-GaO_x channel has not been reported up to now.

Here TFTs with a-GaO_x channel deposited with plasma-enhanced atomic layer deposition (PE-ALD) are discussed. PE-ALD allows for relatively low deposition temperatures (~ 250°C), uniform and conformal films. We recently showed that the current through the a-GaO_x layer can be increased with shorter O_2 plasma exposure times during PE-ALD as it increases the number of sub bandgap defects in the oxide [2]. We present a detailed study of a-GaO_x back-gated TFTs deposited with short (1s) O_2 plasma times to obtain a conductive channel. We discuss the main device characteristics such as subthreshold slope (SS), threshold voltage and ON current and their dependence on the a-GaO_x channel length and thickness (22, 50, 75 nm) with 20 nm ALD Al_2O_3 as gate oxide. Transistors with SS < 150 mV/dec and an ON/OFF ratio of 10^5 have been shown for a channel length of 6 μm. Impact of encapsulation of the GaO_x channel with in situ ALD-grown Al_2O_3 and ex situ PECVD-grown SiO_2 on the hysteresis in the transfer characteristics (drain current as a function of gate voltage) of the devices is investigated. A reduction of the hysteresis is achieved after in situ encapsulation of the devices with 2 nm Al_2O_3. Finally, the effect of post-metal annealing on the device performance is discussed.

[1] J. Kim et al. "Conversion of an ultra-wide bandgap amorphous oxide insulator to a semiconductor", NPG Asia Materials 9, e359 (2017)
[2] H. Kröncke et al., “Effect of O_2 plasma exposure time during atomic layer deposition of amorphous gallium oxide.” Journal of Vacuum Science & Technology A 39, 052408 (2021)

9:20am **EM+MN+TF-ThM-5 Interface Trap State Analysis of ALD-deposited Gate Dielectrics on Gallium Nitride using a Modified C-ψ_s Procedure**, ***Brian Rummel**, L. Yates, C. Glaser, A. Binder, J. Steinfeldt, T. Smith, P. Sharps,* Sandia National Laboratories; *J. Cooper,* Sonrisa Research; *R. Kaplar,* Sandia National Laboratories

The large breakdown electric field strength and high electron saturation velocity of gallium nitride (GaN) make it an attractive semiconductor for high-power and high-frequency applications. GaN-based power systems greatly exceed the power density capabilities of silicon-based systems and currently rival silicon-carbide-based (SiC) systems. However, GaN has been observed to have large interface trap densities at the gate dielectric/semiconductor interface, which inhibits channel mobility in contemporary MIS devices. In addition, typical gate dielectrics are usually deposited by atomic layer deposition (ALD) rather than being thermally grown due to a lack of a high-quality native oxide for GaN. ALD-deposited dielectrics are often associated with a higher concentration of charged oxide defects that promote significant gate leakage currents and induce large shifts in threshold voltages.

Mitigating these defects in wide band gap devices requires reliable characterization techniques suitable for large-scale device fabrication processes. Typical techniques used to characterize the density of interface states for gate dielectrics, such as the high-low method, require unconventionally large probing frequencies to account for fast trap states associated with wide-bandgap materials. The C-ψ_S technique is a quasi-static capacitance-voltage characterization method known for accurately determining surface potentials in MISCAP structures and has been rigorously demonstrated for SiC-based systems. For GaN systems, trap states located at the insulator/GaN interface or within the ALD-deposited dielectric may lead to dynamic charge/discharge processes that are less prevalent in SiC MIS structures with thermally grown oxides and thereby alter the C-ψ_S analysis. In this work, we successfully adapt the C-ψ_S analytical procedure to GaN-based MIS structures by imposing sensible mathematical conditions and accurately measure interface state densities and oxide charges for ALD-deposited gate dielectrics on n-GaN substrates. A range of post-deposition annealing temperatures is investigated to probe how processing conditions may alter defect states associated with alumina or silicon dioxide gate dielectrics. This work highlights recent progress in our endeavor to fabricate robust GaN-based high-power devices and establish reliable wide-bandgap device characterization procedures.

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9:40am **EM+MN+TF-ThM-6 Characterization of Intervalence Band (IVB) Transitions in Boron-Doped Diamond**, ***Souvik Bhattacharya,*** University of Illinois at Urbana Champaign; *J. Boyd,* Case Western Reserve University; *A. Hossein, S. Reichardt,* University of Luxembourg; *N. Maccaferri,* Umea University, Sweden; *O. Shenderova,* Adamas Nanotechnologies Inc.; *L. Wirtz,* University of Luxembourg; *M. Sankaran,* University of Illinois at Urbana Champaign; *G. Strangi,* Case Western Reserve University

Heavily-doped semiconductors are a special class of materials distinct from both their metal and semiconductor counterparts that can exhibit greatly enhanced electrical conductivity^1 and tunable localized surface plasmon resonances (LSPR)$^{2, 3}$. For example, boron-doped diamond is a wide band-gap, p-type semiconductor which has elicited interest for quantum computing^4 and superconductivity^5. Here, we characterized boron-doped diamond (BDD) powders by valence electron-energy loss spectroscopy (VEELS) using a scanning transmission electron microscope to reveal potentially new electronic transitions within the valence band. The diamond samples were synthesized commercially by high-pressure-high-temperature (HPHT) methods and obtained from Adamas Nanotechnologies. Basic materials characterization such as high-resolution transmission electron microscopy (HR-TEM), core-EELS and micro-Raman spectroscopy were conducted to assess the structure and crystallinity. The boron doping level was determined to be ca. 800 pm by modelling the Fano line shape and shifts of the zone center peak at 1332 cm-1. The majority of our study then focused on the low-loss region of EELS (i.e., VEELS) where we observed an intense and relatively broad signal on the shoulder of the zero-loss peak (ZLP) that was completely absent in a similarly synthesized undoped (intrinsic) diamond sample. The feature was found to vary spatially within the body of each particle and inferred to correlate with the distribution of boron atoms along the diamond crystal planes. Ab-initio calculations were carried out in support of the experiments to calculate the loss function from the dielectric function. We find that intervalence band transitions of valence band electrons can lead to the observed VEELS features, and that these transitions can couple to form a "plasmon-like" excitation.

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Fundamental Discoveries in Heterogeneous Catalysis Focus Topic

Room 321 - Session HC+AS+SS-ThM

Bridging Gaps III: Combined Theory and Experiment in Catalysis

Moderators: Liney Arnadottir, Oregon State University, **Sharani Roy**, University of Tennessee Knoxville

8:00am **HC+AS+SS-ThM-1 Mechanistic Understanding and Catalyst Design for Selective Methane Activations**, ***Ping Liu,*** Brookhaven National Laboratory **INVITED**

The development of variable catalysts to promote the activation of methane and control the conversion selectivity has long been a challenge in catalysis. One of the obstacles is the lacking in fundamental understanding of reaction network due to the complexity. Here, the mechanistic study of methane activation to carbon monoxide and/or methanol on metal/oxide and oxide/oxide will be presented using combined Density Functional Theory and kinetic Monte Carlo simulation. Our results not only provide new insight into the mechanism and active sites, but also highlight the importance of confined active site in tuning the binding of intermediates and promoting the catalytic performance.

8:40am **HC+AS+SS-ThM-3 A First Principles Study of Propane Dehydrogenation Reactions on Hydroxyl-Terminated Al_2O_3 Decorated Platinum Surfaces**, ***Sumandeep Kaur**, H. Nguyen, L. Árnadóttir,* Oregon State University

Propylene is precursor of many complex chemicals such as polypropylene, propylene oxide, acrylonitrile etc. which are used in the fabrication of numerous consumer and industrial products. Catalytic dehydrogenation of propane has been proposed as a practical route for propylene production and metal catalysts such as Pt, Pd and Sn have been extensively employed for this purpose. Recent experimental studies have shown that tailoring metal-active sites with atomic layer deposition (ALD) can increase the selectivity of propane dehydrogenation (PDH) towards propylene.^{1} Herein we use DFT and microkinetic modeling to study PDH on Pt surfaces covered with Al_2O_3 to investigate the effect of ALD on PDH. Our primary results show that alumina ALD covers 1/6 of the planar surface Pt(111) blocking all the active sites for propane dehydrogenation while on the step or kink surfaces, (Pt(211), Pt(321), Pt(533)) alumina ALD forms a one-dimensional ribbon like structure along the step or kink atoms, leaning over the lower terrace and leaves room on the upper terrace for the reaction intermediates to interact with the ALD layer and the metal catalyst. These studies on PDH reactions on ALD covered Pt can lead to better understanding on how ALD can be used to tailor catalytic active sites and improve selectivity.

[1] Lu et al. ACS Catal. 2020, 10,23, 13957

9:00am **HC+AS+SS-ThM-4 Atomic-Level Studies of C_2H_4 on clean and Rh_1-Decorated Fe_3O_4(001)***, **Panukorn Sombut**, L. Puntscher, C. Wang, M. Ulreich,* TU Wien, Austria*; M. Meier,* University of Vienna, Austria*; J. Pavelec, Z. Jakub, F. Kraushofer, M. Schmid, U. Diebold,* TU Wien, Austria*; C. Franchini,* University of Vienna, Austria*; G. Parkinson,* TU Wien, Austria

The local binding environment of metal-oxide supported single-atom catalysts (SACs) determines how reactants adsorb and therefore plays a decisive role in catalysis. Here, we study how Fe_3O_4(001)-supported Rh_1 adatoms interact with ethylene (C_2H_4) using density functional theory, combined with temperature-programmed desorption (TPD), x-ray photoelectron spectroscopy (XPS) and scanning tunneling microscopy (STM) techniques. C_2H_4 is the simplest alkene molecule, and thus a model reactant for hydrogenation and hydroformylation reactions. Our study begins with the clean Fe_3O_4(001) surface[1], where C_2H_4 binds weakly. We identify and model different molecule orderings at different coverages that agree nicely with STM images, as well as explain the experimental TPD data. Then, we study C_2H_4 adsorption at 2- and 5-fold coordinated Rh sites at the Fe_3O_4(001) surface, and show that the local environment has a strong effect on the adsorption properties: 2-fold Rh can adsorb two C_2H_4 molecules, while 5-fold Rh can only host a single C_2H_4 molecule. Finally, we investigate coadsorption of C_2H_4 with CO, a vital step towards enabling the hydroformylation reaction, and show that this is feasible only at 2-fold coordinated Rh sites.

1. Bliem, R. *et al.* Subsurface cation vacancy stabilization of the magnetite (001) surface. *Science* **346**, 1215–1218 (2014).

9:20am **HC+AS+SS-ThM-5 How the Support Dictates the Reactivity of FeO_x-Based Single-Atom Catalysts***, **Matthias Meier,*** TU Wien, Austria **INVITED**

Single-atom catalysts are often supported by cheap oxides, such as iron oxides. As a model system[1], magnetite (Fe_3O_4), specifically its (001) facet has been used because it offers stable sites for single-atom adsorption up to high temperatures[2]. Here, I will demonstrate how important the support is for the stability of single-atoms, as well as their catalytic properties.

Rh and Ir single-atoms utilize Fe vacancies in the subsurface of the reconstructed Fe_3O_4(001) unit cell to incorporate into the surface layer. Changing the positions of Fe atoms in the support as part of the incorporation process enables the single-atoms to be accommodated in a more favorable configuration than if they were adsorbing on top of the surface. Their catalytic properties are drastically affected by changes in the atomic environment. Incorporation temperatures vary depending on both coverage and the presence or absence of adsorbates, such as CO.

Changes in the support can affect not only ground states, but also reaction mechanisms and activation barriers. Pt single-atoms become mobile upon CO adsorption, forming dimers, which oxidize CO via a Mars van Krevelen reaction using a surface oxygen atom[3]. The support is temporarily altered, reducing overall activation barriers and permitting CO oxidation otherwise inaccessible at the observed experimental temperatures.

Similarly, subsurface vacancies are also present in Fe_3O_4(111), modifying electronic surface states and allowing again for easy incorporation of single-atoms already at low temperatures, in line with experimental observations.

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11:00am **HC+AS+SS-ThM-10 Modifying Ethane Oxidation Selectivity on the stoichiometric IrO_2(110) surface through anion substitution***, **Aravind Asthagiri,*** The Ohio State University **INVITED**

Selective alkane conversion to high value fuels or chemicals, such as methanol or ethylene, has drawn increasing interest due to abundance of natural gas. Recently, we reported a combined temperature programmed reaction spectroscopy (TPRS) and density functional theory (DFT) study of below room temperature (T ~ 120 K) activation of methane on the stoichiometric IrO_2(110) surface under ultrahigh vacuum (UHV) conditions. Subsequent work also showed that ethane to ethylene selectivity could be increased on IrO_2(110) by creating some proportion of hydrogenated bridging oxygen (O_{br}-H) sites, which limit the oxidative capacity of the surface. This past work suggests that substitution of O_{br} sites with inert species may be an avenue to control selectivity between full and partial oxidation. We have used DFT to explore the effects of Cl substitution of O_{br}. Chlorine is isoelectronic to O_{br}-H and selective Cl substitution of O_{br} has been demonstrated on RuO_2(110) by Over and co-workers. In this work, we apply DFT to explore selective conversion of ethane on Cl-doped IrO_2(110). We find that the Cl-doped IrO_2(110) is still facile in converting ethane to ethylene. In contrast, the ethylene selectivity step shows a strong effect due to Cl doping. Specifically, we find that H atom transfer from ethylene to the saturated O_{br} sites is unfavorable and therefore Cl doping will promote ethylene desorption over further reaction. DFT derived microkinetic simulations show that the selectivity of ethylene peaks at ~60% Cl substitution with increasing Cl substitution reducing the reactivity of ethane. Extending this work to other halogen anion substitutions (F, Br, I) shows that Cl is the optimal dopant. While Br and I favor ethylene desorption over further reaction, these dopants decrease ethane reactivity. In contrast, F dopant does not promote ethylene desorption versus reactivity as effectively as Cl. Current efforts to develop a microkinetic model to explore ethylene selectivity under reaction conditions will be discussed.

11:40am **HC+AS+SS-ThM-12 HC Graduate Student Finalist Talk: Insight into Subsurface Adsorption and Reconstruction of Ag(111) Deduced from a Lattice-Gas Model and Monte Carlo Simulations***, **Carson Mize,*** University of Tennessee Knoxville*; L. Crosby,* Joint Institute for Computational Sciences; University of Tennessee Knoxville*; E. Lander, S. Roy,* University of Tennessee Knoxville

Gas-phase surface models are a beneficial, theoretical tool for providing qualitative insight into elementary steps of surface chemistry. Elementary steps, like adsorption, play a crucial role in many chemical phenomena like surface reconstruction and industrial heterogeneous catalysis. While there exist many previously developed gas-phase adsorption models, most models are limited to low adsorbate coverages due to the computational cost required to produce high coverage models. To investigate adsorption over a broad range of adsorbate coverages on a crystalline solid, we have developed a lattice-gas adsorption model that includes surface and subsurface adsorption, tunable interaction parameters calculated with density functional theory, and larger scale modeling with Monte Carlo simulations. This model has been applied to study oxygen adsorption on a Ag(111) surface, due to experimental findings suggesting the possibility of subsurface-adsorbed oxygen species. Our first model iteration included only strongest binding sites for each region and our simulations indicated greater oxygen accumulation in the second subsurface than the first subsurface in total coverages in excess of 0.375 monolayer (ML). Our second model iteration included all high symmetry sites in each region and found the same qualitative results as the first model using canonical Monte Carlo distributions. Additionally, current grand canonical distributions suggest some subsurface oxygen adsorption exists under temperatures of 475 – 550 K and pressures of 1 – 2 bar, which are typical industrial conditions for catalysis with these systems. Our current model includes adding Ag – Ag and Ag – O interactions to model surface reconstruction, as our previous models only included the unreconstructed silver lattice. This iteration will allow us to study the role of surface and subsurface oxygen in inducing well-known surface reconstructions of Ag(111), such as p(4 × 4) and c(4 × 8) lattices, as a function of surface temperature and oxygen pressure using Monte Carlo simulations.

12:00pm **HC+AS+SS-ThM-13 Measuring and Predicting a Key Catalyst-Performance Descriptor for Supported Metal Nanoparticle Catalysts: Metal Chemical Potential***, **Charles T. Campbell**, J. Rumptz, K. Zhao,* University of Washington

Metal nanoparticles supported on high-area oxides and carbons form the basis for many catalysts and electrocatalysts. Their activity and stability depend on both particle size and choice of support. The chemical potential of the metal atoms in the catalyst material quantifies their stability and is a convenient descriptor that captures the effects of both the nanoparticle size and the support material on both surface reactivity and sinter resistance.[1,2] This chemical potential enters quantitatively into the rate equations for sintering, making a negative contribution to the activation energy.[2] Numerous experimental and theoretical studies have also found that the stability of metal atoms in catalyst materials, including alloys, correlates with their binding energies to adsorbates, whereby surface metal atoms that are more weakly bound to the solid interact more strongly with small adsorbates like O, CO, -OH and $-CH_3$.[1-3] It is thus desirable to develop methods to predict how metal chemical potential depends on particle size and support. Herein, we report calorimetric measurements of: (1) metal chemical potential as a function of particle size and support, and (2) the adhesion energy of the solid metals to different oxide and carbon supports.From these, we have identified predictive correlations of: (1) metal chemical potential in supported nanoparticles as a function of the particle size and the adhesion energy of the particle to the support, and (2) the dependence of this adhesion energy upon the metal element in the catalyst for oxide supports.

Work supported by DOE-OBES Chemical Sciences Division.

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Advanced Ion Microscopy and Ion Beam Nano-engineering Focus Topic
Room 301 - Session HI+AS-ThM

Advanced Ion Microscopy & Surface Analysis

Moderators: Armin Golzhauser, Bielefeld University, Germany, **Shida Tan**, Intel Corporation

8:00am **HI+AS-ThM-1 Defect Engineering on the Atomic Scale with the Helium Ion Microscope***, **Frances I. Allen,*** UC Berkeley **INVITED**

The use of ion beams to tune the properties of materials through the introduction of defects is a well-established technique. In this area, focused ion beam microscopes have the advantage that they allow the researcher to irradiate materials locally in a highly controlled manner. Over the last 15 years, the Helium Ion Microscope (HIM) has been employed for a range of defect engineering applications, in particular concerning thin films and 2D materials. Properties tuned include electrical, magnetic, optical and thermal behavior, achieved by varying the concentration of defects and local disorder, controlled by varying the ion dose [1]. In the case of freestanding atomic monolayer materials, it has been shown that irradiation with helium (and neon) ions using the HIM in raster mode (as opposed to e.g. spot mode), can form single vacancy defects and vacancy defect clusters due to single-ion hits [2,3]. Such sub-nanometer pores have applications in gas separation [4] and for selective ion transport in liquid [5]. In this talk, I will discuss the fabrication of sub-nanometer pores in 2D materials using the HIM. I will present characterization results from Raman spectroscopy and high-resolution transmission electron microscopy, and will also discuss the merits of multi-step fabrication workflows in which vacancy "seeds" are first introduced into the 2D material by ion irradiation, that are then expanded into the final nanopores of desired size and shape by plasma treatment and/or electron beam irradiation.

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[3] P. Maguire, D. S. Fox, Y. Zhou, Q. Wang, M. O'Brien, J. Jadwiszczak, C. P. Cullen, et al. 2018. "Defect Sizing, Separation, and Substrate Effects in Ion-Irradiated Monolayer Two-Dimensional Materials." *Physical Review. B, Condensed Matter* 98 (13): 134109.

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[5] A. Smolyanitsky, E. Paulechka, and K. Kroenlein. 2018. "Aqueous Ion Trapping and Transport in Graphene-Embedded 18-Crown-6 Ether Pores." *ACS Nano* 12 (7): 6677–84.

8:40am **HI+AS-ThM-3 Effects of Defects and Si Doping on Ion Motion in TaOx Bilayer Memristors***, **Matthew Flynn-Hepford,*** University of Tennessee Knoxville*; J. Keum, I. Kravchenko, S. Randolph, A. Ievlev, B. Sumpter,* Oak Ridge National Laboratory*; M. Marinella,* Arizona State University*; O. Ovchinnikova,* Oak Ridge National Laboratory

TaOx materials have promising properties for memristive applications such as long state retention time and consistent resistive switching.If the mechanism of the resistive switching can be controlled, these materials could be the foundation for the next generation of neuromorphic computing. A material design approach was implemented with the goal of lowering the operational voltage of these devices.Radial distribution functions (RDF) of the modeled TaOx materials with added defects and Si doping were used to predict the bonding strength of the materials.Experimentally, in order to increase ion mobility, defects were introduced into the active layer by He ion irradiation.Local strong bonding was induced in the form of local Si doping by Si irradiation, in an attempt to induce ion mobility channels where ion motion can be better controlled.In order to probe the mechanism of this resistive switching, conductive atomic force microscopy (c-AFM) and kelvin probe force microscopy (KPFM) were used to induce ion motion in the thin films and probe the change in surface potential, respectively.Specially resolved time-of-flight secondary ion mass spectroscopy (ToF-SIMS) was used to probe the chemical change in the film with applied tip bias.These c-AFM and KPFM experiments along with ToF-SIMS were used to probe the locally defected and Si-irradiated areas in order to better understand the effects of defects and Si doping on ion mobility in TaOx bilayer memristors.

9:00am **HI+AS-ThM-4 Advantages of Using Helium Ion Microscopy for Morphological Analysis of $BiScO_3$-$PbTiO_3$ Piezoelectric Ceramics***, S. Chen, A. Bunevich, Y. Yuan, **Karen Kavanagh**, Z. Ye,* Simon Fraser University, Canada

Piezoelectric materials can convert mechanical energy into electrical and vice versa. Imaging by Scanning Electron Microscopy (SEM) is commonly used for initial morphological analysis of the grain size, uniformity and porosity, properties that correlate with the piezoelectric quality of interest. However, piezoelectric ceramic is highly insulating, requiring a conductive coating to inhibit charging while imaging through secondary electron collection in most SEMs. Thus, SEM images may not be representative of the sample surface. We have found that there are numerous advantages to using Helium Ion Microscopy (HIM) instead. In a HIM, a positively-charged focussed He ion beam is used to excite secondary electrons, with sample charging neutralized by a simultaneous, large-area electron flood gun. Samples are analysed directly without any surface modification, enabling rapid comparisons of a sintered batch for selection of the best quality ceramic for electrical testing. Higher resolution is achieved for better images of grain boundaries and textural irregularities that are not visible by SEM. In this talk, we will compare SEM and HIM secondary electron images of various compositions of $BiScO_3$-$PbTiO_3$ ceramics, a high temperature piezoelectric material. We will show examples of nanometer-wide ceramic grain boundaries and triple points that were not visible using SEM. Grain boundaries are regions of changes in the lattice structure that have significant implications for piezo and other electronic properties. We have found HIM images to show surface topography and regions of dramatically different contrast that are invisible in the SEM. Furthermore, the lack of conductive coating allows us to see variations in the grain boundary itself, which may explain why piezoelectric properties fluctuate with region in a single sample. Ceramics with large grains (> 20 mm) and flat surfaces correlated with high ferroelectricity at 200°C, with a $P_{max} = 282$ mC/cm^2. These samples were also more physically robust and able to be poled at higher temperatures and voltages than previous samples of the same composition, improving their piezoelectric properties. Incorporating HIM into the design and synthesis process allows us to quantify the effects of factors such as sintering temperature and die conditions on the physical quality of the ceramic, which ultimately determines its electronic properties and the feasibility of material commercialization.

Acknowledgments

This work is supported by the Natural Science and Engineering Research Council of Canada (NSERC grant RGPIN-2017-06915).

9:20am **HI+AS-ThM-5 Low-Energy Ion Implantation - Range Comparisons between Theory and Experiment***, **Michael Titze,*** Sandia National Laboratories*; J. Poplawsky,* Oak Ridge National Laboratory*; A. Belianinov, E. Bielejec,* Sandia National Laboratories

The continued decrease in size of microelectronic devices has created a need for shallower implanted dopant layers. With the recent discovery of two-dimensional (2D) materials, the ultimate limit for shallow layer implant is incorporating material into a single monolayer. Multi-specie focused ion beams (FIB) can operate with a variety of ion species and enable direct-write implantation of specific ions tailored for an exact application. Prior to any ion irradiation experiment, the range of ions in the material needs to be calculated, often predicted by using freely available Stopping and Range of Ions in Matter (SRIM) simulation.

SRIM simulations are in excellent agreement with experiment for high energy light ions, however, for low energy heavy ions, discrepancies between SRIM and observed experimental values have been reported. We use Rutherford backscattering spectrometry (RBS), Secondary ion mass spectrometry (SIMS) and Atom-probe tomography (APT) to measure the depth of heavy ions in silicon following FIB implantation with energies from 1 – 150 keV. The resolution limit of RBS and SIMS is on the order of nanometers, comparable to the implantation depth for few keV ion implants, requiring the use of APT for measuring lowest energy implants because APT is capable of almost angstrom resolution in the 100 direction of single crystalline Si. The difference between SRIM and experimental result is < 10 nm for all investigated ion energies, however due to the low overall range of the ions, the relative error is larger for lower ion energies with 1 keV as the minimum energy investigated showing > 500 % relative discrepancy.

This work was performed, in part, at the Center for Integrated Nanotechnologies, an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science. Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International, Inc., for the U.S. DOE's National Nuclear Security Administration under contract DE-NA-0003525. The views expressed in the article do not necessarily represent the views of the U.S. DOE or the United States Government.APT research was supported by the Center for Nanophase Materials Sciences (CNMS), which is a US Department of Energy, Office of Science User Facility at Oak Ridge National Laboratory.

11:00am **HI+AS-ThM-10 Correlative Microscopy Using HIM and HIM/SIMS***, **Florian Vollnhals,*** Institute for Nanotechnology and Correlative Microscopy - INAM, Germany*; G. Sarau,* Fraunhofer Institute for Ceramics Technology and Systems - IKTS, Germany*; A. Kraus,* Institute for Nanotechnology and Correlative Microscopy - INAM, Germany*; S. Christiansen,* Fraunhofer Institute for Ceramics Technology and Systems - IKTS, Germany **INVITED**

The Helium Ion Microscope (HIM) has changed the world of charged particle microscopy [1]. The attainable spot sizes have enabled advances in imaging as well as nanotechnological applications such as ion beam lithography, nanopatterning or material modification.

An area that has been challenging for HIM, especially in comparison to scanning electron microscopy (SEM), is sample analysis beyond secondary electron (SE) imaging. While most SEMs are equipped with some form of X-ray detection systems (e.g., EDX) for chemical analysis, and many more analytical modes available for further characterization of physical or chemical sample properties, such capabilities have been limited for HIM [3].

The HIM community has made considerable efforts to improve this situation by introducing ion beam specific detection tools like Rutherford backscattering (RBS), Scanning Transmission Helium Ion Microscopy (STHIM) or Secondary Ion Mass Spectrometry (SIMS) using the neon ion beam provided by the latest generation ORION NanoFab HIM [2].

In HIM-SIMS, the focused ion beam is scanned across and thus sputters the surface, resulting in the emission of atoms and ions. The ions are collected and guided to a mass analyzer, allowing for the detection of ions and small clusters ranging from light elements like hydrogen, lithium and boron to heavy elements like Lead. Especially the detection of lithium is a valuable new tool for battery research.

Recently, the SIMS detection system developed by Wirtz et al. at Luxembourg Institute of Technology (LIST) has been upgraded from four individual detectors into a prototype focal plane detector within the npSCOPE project (npscope.eu, funded by the European Commission), allowing for the detection of many masses in parallel, which is beneficial for many applications for which a compositional analysis is required [3].

In addition to the detector development efforts at LIST, a focus has been set on the development of workflows for correlative microscopy using the HIM in a context of additional analytical modalities. The correlation of high resolution HIM and HIM-SIMS imaging with complementary analytical modalities like atomic force microscopy, optical or Raman microscopy to allow for new insights and overcome some of the limitations of the individual tools [4].

This contribution aims at showcasing applications of HIM-SIMS and offers some insights into correlative microscopy workflows involving the HIM.

[1] Ward et al., J. Vac. Sci. Technol. B 24 (2006) 2871

[2] Wirtz et al., Annu. Rev. Anal. Chem. 12 (2019) 523

[3] Audinot et al., Reports Prog. Phys. 84 (2021) 105901

[4] Vollnhals et al., Anal. Chem. 89 (2017) 10702

11:40am **HI+AS-ThM-12 Electronic vs. Nuclear Sputtering of Coronene***, **Lars Breuer,** T. Heckhoff, M. Herder,* University of Duisburg-Essen, Germany*; H. Tian, N. Winograd,* The Pennsylvania State University*; A. Wucher,* University of Duisburg-Essen, Germany

Electronic sputtering induced by swift heavy ion (SHI) irradiation of solids has been suggested as a relatively soft desorption mechanism for intact molecules in Secondary Ion Mass Spectrometry (SIMS). In order to evaluate the prospects of this "MeV-SIMS" technique as compared to the standard SIMS methodology utilizing nuclear sputtering with projectile energies in the keV range, we have performed a case study using time-of-flight (ToF) mass spectrometry to detect both ionized and neutral particles sputtered from a coronene film. In particular, secondary ion and neutral mass spectra obtained under 4.8 MeV/u Ca, Bi and Au ion impact were compared with those measured under irradiation with keV Ar, C_{60} and Ar_{1500} ions. While secondary ions were directly detected using a reflectron ToF spectrometer, sputtered neutral particles were post-ionized using two different laser photoionization schemes, namely vacuum ultraviolet single photon ionization at 157 nm and infrared strong field ionization at wavelengths between 800 and 1300 nm, respectively. The measured spectra are interpreted in terms of partial sputter yields, fragmentation patterns, emission velocity distributions and ionization probabilities with emphasis on the emission and/or formation of intact molecular ions.

The obtained data clearly demonstrate that the MeV-induced electronic sputtering process results in much cleaner molecule spectra than the keV-induced nuclear sputtering process even if cluster projectiles are used in the keV experiment. In particular for the Ca SHI and SPI post-ionization, the measured spectra are completely dominated by unfragmented neutral coronene molecules detected at m/z 300, followed by some fragmentation via the loss of one or more hydrogen atoms. Interestingly, the spectra measured under SHI impact are even cleaner than those measured under thermal evaporation conditions, thereby illustrating a fundamental difference between macroscopic thermal evaporation and the electronic sputtering process. Comparing the secondary neutral and ion spectra, one finds an ionization probability of the intact molecule of the order of 1 % under SHI impact, which may be slightly higher than that measured under keV C_{60}^+ ion impact (several 10^{-3}). Apart from the hugely different fragmentation characteristics, no significant difference is found between SHI and keV cluster ion impact regarding the emission velocity distributions of the emitted molecules, thereby indicating that the measured signals largely represent the respective partial sputter yields.

12:00pm **HI+AS-ThM-13 Scanning Transmission Helium Ion Microscopy-How Does It Compare to TEM?***, **Annalena Wolff,*** Caltech*; R. Fieth,* QUT, Australia

This work explores the HIM's analysis capabilities of unstained biological samples using a self-built dark field scanning transmission ion microscopy holder. For thin enough samples, such as thin sections of biological specimen on TEM grids, the high energy helium ions can penetrate through the sample. While the ion transverses through the thin foil, it undergoes collisions with the sample atoms and is deflected. The ion exits the sample at a deflection angle which is specimen thickness, ion energy as well as sample material dependent. The deflection angle can be determined using Monte Carlo simulations. The freeware program Stopping and Range of Ions in Matter was used in this work. This effect can be used to design a dark field scanning transmission ion microscopy holder (DF-STIM). The holder design is based on a previously reported experiment [1]. In principle, ions, which are deflected by a specific angle hit a metal conversion plate, which is mounted at a specified distance h below the sample. Here, the transmitted ions create a secondary electron signal which can be collected by the HIM's Everhart-Thonley Detector. Ions which are deflected less than the acceptance angle enter a hole in the holder which his located directly below the specimen. This hole acts as a Faraday cup. For this case, no secondary electron signal is created. For biological samples, areas with higher carbon density create signal while areas with lower carbon density create less signal and can this be distinguished in the DF STIM image.

The DF STIM holder is tested by imaging stained and unstained biological samples and the results are compared to TEM measurements.

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[2] Dr. Crystal Cooper is thanked for the many useful discussions and the sample preparation suggestions.

Magnetic Interfaces and Nanostructures Division
Room 330 - Session MI+2D+TF-ThM

Quantum Materials (2D)

Moderator: Zheng Gai, Oak Ridge National Laboratory

8:00am **MI+2D+TF-ThM-1 Exploration of Two Surfaces Observed in Weyl Semimetal BaMnSb$_2$**, ***Zheng Gai**, Q. Zou,* Oak Ridge Natinal Laboratory*; S. Huang,* University of South Carolina*; W. Ko, M. Fu,* Oak Ridge Natinal Laboratory*; Y. Yang, K. Zhao,* Louisiana State University*; S. Crittenden,* University of South Carolina*; E. Plummer,* Louisiana State University*; R. Jin,* University of South Carolina

Single crystalline BaMnSb$_2$ is considered as a 3D Weyl semimetal with the 2D electronic structure containing Dirac cones from the Sb sheet. The unique surface electronic structure can be probed by techniques such as angle-resolved photoemission spectroscopy (ARPES) and scanning tunneling microscopy/spectroscopy (STM/S). However, these techniques require an in-depth understanding of the surface structure and electronic properties. We report experimental investigation of low-temperature cleaved BaMnSb$_2$ surfaces using STM/S and low energy electron diffraction (LEED). By natural cleavage, we find two terminations: one is Ba1 (above the orthorhombic distorted Sb sheet) and another Sb2 (at the surface of the Sb/Mn/Sb sandwich layer). Both terminations show the 2 × 1 surface reconstructions, with drastically different morphologies and electronic properties, however. The reconstructed structures, defect types and nature of the electronic structures of the two terminations are extensively studied. The quasiparticle interference (QPI) analysis also reveals that the surface-projected electronic band structures strongly depend on the surface termination. The existence of defects can greatly modify the local density of states to create electronic phase separations on the surface in the order of tens of nm scale. Our observation on the atomic structures of the terminations and the corresponding electronic structures provides critical information towards an understanding of topological properties of BaMnSb$_2$.

8:20am **MI+2D+TF-ThM-2 Properties of Mn$_3$Sn Films Grown on Sapphire Substrates Using Molecular Beam Epitaxy**, ***Sneha Upadhyay,*** Ohio University*; T. Erickson, D. Ingram,* Ohio University*; K. Sun,* The University of Michigan , Ann Arbor*; A. Smith,* Ohio University

The kagome antiferromagnet Mn$_3$Sn is a fascinating material because it's one of the rare antiferromagnets that exhibits large anomalous Hall and Nernst effects. This opens a new area of research using functional antiferromagnets[1], but for future device applications, it requires fabricating high-quality thin films. There are reports of the controlled growth of Mn$_3$Sn on substrates like *m*-plane sapphire,[2] Pt/Al$_2$O$_3$ (0001)[3,] and others using sputtering growth, but this often can result in polycrystalline films. In this work, we investigate the growth of Mn$_3$Sn films on *c-plane* sapphire substrates using molecular beam epitaxy. Effusion cells are used for Mn and Sn sources which are calibrated using a quartz crystal thickness monitor. The growth is monitored *in-situ* using reflection high energy electron diffraction and *ex-situ* measurements are carried out using X-ray diffraction, Rutherford backscattering, and cross-sectional scanning transmission electron microscopy. The samples are grown at 500 ± 9°C and 416 ± 9 °C with an Mn: Sn atomic flux ratio of 3.2: 1 on *c-plane* sapphire substrates for 60 mins. We observe streaky RHEED patterns at both temperatures indicating high-quality crystalline growth with 2 different orientations, (0001) and (11-20), which are also backed up by the XRD spectra. STEM verifies ~3:1 Mn to Sn stoichiometry but also reveals discontiguous films. After optimizing the growth conditions, the next phase of the study is to begin *in-situ* scanning tunneling microscopy and spin-polarized STM studies of the structural, electronic, and magnetic properties of the *as-grown* Mn$_3$Sn surfaces, and in this presentation, we plan to present initial results.

The authors acknowledge support from the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering under Award No. DE-FG02-06ER46317. The authors would like to thank Dr. Stinaff and his students for back coating the sapphire substrates.

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8:40am **MI+2D+TF-ThM-3 Interfacial Magnetism in Oxide Heterostructures**, ***Alex Demkov,*** The University of Texas at Austin **INVITED**

New functionalities and unexpected electronic structures can emerge in artificially engineered complex oxide heterointerfaces due to the coupling of multiple physical properties such as ferroelectricity, ferromagnetism, conductivity, charge transfer, etc. Here, we discuss heterointerfaces involving perovskite oxides SrTiO$_3$, LaAlO$_3$, and BaTiO$_3$, as well as a rock salt ferromagnetic semiconductor EuO. Combining theoretical analysis, experimental growth, and characterization techniques with atomic level resolution, we highlight some of these intriguing emergent interfacial phenomena. We consider several means of creating a two-dimension carrier gas, through band offset engineering, polarization doping, and oxygen vacancy doping. In addition, we also discuss ways of manipulating these electron/hole gases and their potential applications in new electronic devices.

Starting from the pioneering discovery of a 2DEG at the LAO/STO interface, interfaces of transition metal oxides have been at the center of many theoretical and experimental studies. This two-dimensional carrier gas is rather different from the one occurring in semiconductor heterostructures. Its origins and mechanisms of spatial localization are rather complex. Thanks to modern experimental and theoretical techniques, one can identify which of these mechanisms are actually present at a given interface. In some cases, we can also tailor the choice of specific materials where one mechanism dominates, allowing us to study that particular mechanism in more detail.

Owing to relatively large band gaps and the presence of occupied as well as empty ***d*** and***f*** states, the oxide interfacial 2DEG shows a higher degree of spatial confinement.It is a unique physical system where, in the span of just about a nanometer, one can create strong interactions between multiple order parameters leading to phenomena that in the bulk are either very small or forbidden by symmetry. Besides the fundamental physics interest, these multi-functional interfaces may one day be utilized for technological applications.

The work has been supported by the Air Force Office of Scientific Research under grants FA9550-18-1-0053 and FA9550-12-10494, the Texas Advanced Computing Center, and by the National Science Foundation under grants IRES–1358111.

9:20am **MI+2D+TF-ThM-5 Epitaxial 2D Van Der Waals Magnets**, ***Roland Kawakami,*** Ohio State University **INVITED**

In this talk, I will discuss our latest advances on the epitaxial growth of 2D van der Waals (vdW) magnets and their integration with topological insulators (TI). This work is motivated by the realization of topological phases such as the quantum anomalous Hall effect and highly efficient spin-orbit torque produced by TIs. We have focused on integrating 2D magnets $MnSe_2$, Fe_3GeTe_2 (FGT) and $CrGeTe_3$ (CGT) with TIs Bi_2Se_3 and Bi_2Te_3.

Our initial studies of $MnSe_2$ growth on Bi_2Se_3 showed a tendency for the interdiffusion of Mn into the Bi_2Se_3. While this was initially undesirable, this ultimately led to the synthesis of $MnBi_2Se_4$ (MBS), a new magnetic topological insulator. This is a vdW material with septuple layer (Se-Bi-Se-Mn-Se-Bi-Se) base units, similar to its cousin $MnBi_2Te_4$ (MBT). However, the vdW phase is not the thermodynamically stable phase and bulk crystals do not exist, so the epitaxial stabilization of MBS creates the opportunity to explore the magnetic and topological properties of this material. We find that MBS is a layered antiferromagnet, similar to MBT, but a difference is that the magnetic moments lie in the plane of the film. Angle resolved photoemission experiments show the presence of a topological surface state with Dirac dispersion.

For bilayers of 2D magnets and TIs, we have focused on FGT and CGT films. A key step has been the optimization of FGT by studying its growth on Ge(111) substrates. Here, we learned that kinetics play an important role in the epitaxial growth. By varying the deposition rate, we control the formation or suppression of an initial tellurium-deficient non-van der Waals phase (Fe3Ge2) prior to realizing epitaxial growth of the vdW FGT phase. Using cross-sectional scanning transmission electron microscopy and scanning tunneling microscopy, we optimize the FGT films to have atomically smooth surfaces and abrupt interfaces with the Ge(111) substrate. The magnetic properties of our high quality material are confirmed through magneto-optic, magnetotransport, and spin-polarized STM studies. Importantly, this demonstrates how the interplay of energetics and kinetics can help tune the re-evaporation rate of chalcogen atoms and interdiffusion from the underlayer. Utilizing these insights, we have developed the growth of FGT and CGT on Bi_2Te_3 for the integration of 2D magnets with TIs.

11:00am **MI+2D+TF-ThM-10 Hybrid Superconductor-Semiconductor Device***, **Sergey Frolov,*** University of Pittsburgh **INVITED**

Research into the generation, confirmation and manipulation of Majorana zero modes has brought heightened interest to hybrid materials systems made of fairly conventional components such as s-wave superconductor metals and semiconductors. The game in this arena is to carefully tailor the properties of an electronic device to make possible the observation of exotic physics such as topological superconductivity. The main lesson that we have learned is that the path to any plausible discovery lies through painstakingly careful and very deep understanding of the materials properties and device fabrication conditions. This being true for such a standard set of materials, the lesson certainly applies to more exotic compounds.

In this talk I will briefly summarize the status of the search for Majorana modes in superconductor-semiconductor hybrid devices. I will also highlight other unusual phenomena that arise in these systems such as higher order Josephson effects, time-reversal symmetry broken Josephson current phase relations. I will also show how these materials can be used to build quantum circuits with enhanced functionality, not necessarily arising from topological protection.

11:40am **MI+2D+TF-ThM-12 Magnetotransport in Graphene/$Pb_{0.24}Sn_{0.76}Te$ Heterostructures: Finding a Way to Avoid Catastrophe***, G. Stephen,* Laboratory for Physical Sciences*; I. Naumov,* Howard University*; N. Blumenschein, L. Sun, **Jennifer DeMell,*** Laboratory for Physical Sciences*; S. Shirodkar, P. Dev,* Howard University*; P. Taylor,* Army Research Laboratory*; J. Robinson, P. Campbell,* Naval Research Laboratory*; A. Hanbicki, A. Friedman,* Laboratory for Physical Sciences

While heterostructures are ubiquitous tools to enable new physics and device functionalities, the palette of available materials has never been richer. Combinations of two emerging material classes, 2D materials and topological materials, are particularly promising because of the wide range of possible permutations that are easily accessible. Individually, both graphene and $Pb_{0.24}Sn_{0.76}Te$ (PST) are widely investigated for spintronic applications because graphene's high carrier mobility and PST's topologically protected surface states are attractive platforms for spin transport. Here, we combine monolayer graphene with PST and demonstrate a hybrid system with properties enhanced relative to the constituent parts. Using magnetotransport measurements, we find carrier mobilities up to 20,000 cm^2/Vs and a magnetoresistance approaching 100%, greater than either material alone. We also establish there are two distinct transport channels and determine a lower bound on the spin relaxation time of 4.5 ps. The results can be explained using the polar catastrophe model, whereby a high mobility interface state results from a reconfiguration of charge due to a polar/non-polar interface interaction. Our results suggest that proximity induced interfaces states with hybrid properties can be added to the still growing list of remarkable behaviors in these novel materials.

Plasma Science and Technology Division
Room 315 - Session PS-ThM

Plasma Processing for Advanced Semiconductor Devices

Moderators: John Arnold, IBM Research Division, Albany, NY, **Kenji Maeda**, Hitachi High Technologies America Inc.

8:00am **PS-ThM-1 Dry Etch Solution to a Challenge in Si/SiGe Dual Channel Process Integration***, **Yohei Ishii**[1],* Hitachi High-Tech America, Inc.*; R. Sugano,* Hitachi, Ltd., Japan*; Y. Lee, W. Wu,* Taiwan Semiconductor Research Institute, Taiwan*; L. Kovatch,* Hitachi High-Tech America, Inc.*; K. Maeda, M. Miura,* Hitachi High-Tech Corporation, Japan **INVITED**

Continuous improvement in terms of device scaling has been made in order to follow Moore's law. Transition from planar structure into Fin-type Field Effect transistor (FinFET) was incorporated so as to obtain higher drive current and lower leakage. To further enhance the electrical properties, introduction of high mobility channel material in P-FET [1], silicon germanium (SiGe), was utilized, while maintaining silicon (Si) in N-FET. This brought up new challenges that are related to not only etch controllability between silicon and silicon germanium, but also interface quality on SiGe channel.

In this presentation, we will discuss the etching challenge in the dual channel fin application. In the fabrication scheme, Si and SiGe need to be etched simultaneously, which requires etched rate controllability between the two materials. However, SiGe etch rate is higher than Si under halogen chemistries. In this investigation, we developed a novel plasma process that controls the etching characteristics (i.e., higher Si etch rate than SiGe) [2], leading to Si-SiGe etched amount control. We will reveal the etch mechanism of the plasma process utilizing surface analysis and ab-initio calculation.

In addition to the etch control, interface condition between gate oxide and SiGe channel is also critical. Sub-threshold can be improved by reducing interface trap density at the interface [3], which can be achieved by obtaining a Si-rich surface. There are a few conventional methods that can achieve a Si-rich surface on SiGe such as atomic layer deposition of Si cap over SiGe [4] and GeOx scavenging [5]. All of these require high temperature processes that cause issues such as atomic diffusion and strain relaxation. In this investigation, we will introduce a plasma treatment at room temperature that creates Si-rich surface. We investigated the mechanism of the surface modification into a Si-rich surface on SiGe under the plasma treatment [6]. We will also present how this has an impact on reducing interface trap density in terms of electrical performance.

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[6]. Y. Ishii, et. al., IEEE J. Electron Devices Soc. **7**, 1277 (2019)

8:40am **PS-ThM-3 Investigation into the Effect of Plasma-Deposited $SiCl_4/O_2$ Chamber Wall Coatings on the Selective Fluorine-Based Etching of TaN with Respect to Polycrystalline Silicon and Silicon Oxide***, **Ivo Otto IV**,* Tokyo Electron Ltd.*; C. Vallée,* SUNY Polytechnic Institute*; K. Yu, S. Kal, A. Mosden, P. Biolsi,* Tokyo Electron Ltd.

Tantalum nitride (TaN) is widely used as a crucial component of diffusion barriers within the back-end-of-the-line (BEOL) because of its strong dielectric adhesion and ability to scale low in-plane resistivity and diffusion-blocking capability to sub-5 nm thicknesses. In order to create the BEOL interconnect superstructure, a cyclical process of conductor and liner deposition and etching, followed by dielectric capping must be completed. In this paper, we will explore the use of inductively-coupled plasma (ICP) discharges containing NF_3/Ar, NF_3/O_2/Ar, and $NF_3/SiCl_4$/Ar mixtures for the isotropic, dry etching of TaN; relying on radically-based etch, without non-

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[1] **2020 PSTD Young Investigator Award Winner**

selective ion bombardment. The aforementioned radically-based process is sensitive to chamber wall condition during the etching process; therefore, we considered that such methods often employ wall coatings in order to achieve superior etch uniformity and wafer-to-wafer reproducibility. This process is outlined in Figure 1; comparing the process utilizing coating and without utilizing coating. PATH A includes chamber conditioning without coating followed by the etching of the sample wafer, while PATH B includes the application of coating prior to sample wafer processing. The mechanism of $SiCl_4$ and O_2 PECVD of SiO_2 has been extensively studied, while the impact of the coating itself on metal and metal nitride etching has not been so well explored. The aforementioned dry-etching chemistries for the removal of TaN are compared with and without using a $SiCl_4/O_2$ chamber coating: comparing the etching process of the TaN film and etch selectivity to polycrystalline silicon and silicon dioxide. In-situ optical emission spectroscopy is utilized to find that the $SiCl_4/O_2$ chamber coating reacts with the ICP discharge to modify relative species densities when compared to a discharge without the chamber coating applied. Furthermore, modification does not only occur within the discharge, but at the film surface, where we use spectroscopic ellipsometry (SE) to find the etching selectivity of the TaN film is significantly changed with respect to the polycrystalline silicon and silicon oxide upon coating application. O_2 and $SiCl_4$ are separately added directly to the plasma discharge in order to characterize the effect of coating constituent gases and to ascertain if a similar affect to coating addition could be attained with direct addition of O_2 or $SiCl_4$ to the discharge. X-ray photoelectron ellipsometry is utilized in order corroborate SE findings, but to also give an idea of the fluorine-based etching pathway the TaN undergoes towards achieving full removal.

9:00am **PS-ThM-4 Influence of Aspect Ratio on Isotropic Etch Process: A Case Study with SiCN Material**, *P. Luan, **Andrew Nolan**, Y. Yoshida, Y. Han, P. Biolsi,* TEL Technology Center, America, LLC, USA; *K. Ken, N. Ikezawa,* Tokyo Electron Ltd., Japan

Etching of trenches and holes into low-k dielectrics is an indispensable process in very-large-scale integration (VLSI) applications. As the critical dimension (CD) size shrinks aggressively with the advancement of technology nodes, the same etch amount (EA) leads to significantly increased aspect ratio (AR, calculated by EA/CD). In this work, we use SiCN as an exemplary low-k dielectric to investigate the effect of AR in isotropic etch processes where F-containing neutrals are the dominant etchant and the effects from ions are minimized. Blanket SiCN films and Si shadow mask were used to form a testing structure with which AR ranging from 0:1 to 70:1 can be evaluated. The etch amount of SiCN materials and their refractive index were evaluated using Spectroscopic ellipsometry (SE). The surface composition pre- and post-etch processes were examined by X-ray photoelectron spectroscopy (XPS), and Fourier transform infrared spectroscopy (FTIR) at various ARs. We found that the etch rate and surface composition inside the shadow mask are dramatically different from those outside, which reflects the effect of ions on SiCN etching. With higher AR, the etch rate of SiCN reduces whereas the surface composition of the etched SiCN film shows the formation of F-containing etch byproduct concentrated in the AR range between 15:1 and 45:1. The etch byproduct shows a characteristic XPS N1s peak at 403.8 eV, a Si2p peak at 105.1 eV, and a large amount of Fluorine. The accumulation such byproduct in this particular AR range could be resulted from the transport property of neutral-reactants from plasma and the lack of ion bombardment.

11:00am **PS-ThM-10 Plasma Etch Fundamentals and Engineering: Advancing Interconnect Scaling**, ***Theo Standaert,*** IBM Research Division, Albany, NY **INVITED**

Since IBM introduced Cu in 1997, the scaling of these interconnects has been relentless for more than two decades. Hundreds of miles of wiring are now deployed in a mindboggling small footprint for the most advanced computer chips, completing the electronic network for billions of transistors. Plasma etch has been and continues to be one of the essential process steps responsible for interconnect scaling. This review starts with some personal experiences as a young engineer, shortly after graduating in the field of plasma etch and surface science. Science and engineering are very different domains. Both are key for advancing and developing new technologies. In case of plasma etch engineering, one must understand the other processes and their constraints, both up- and down-stream in the manufacturing flow. Problems or challenges are rarely confined to a single process or sector. An example of isolated via etch-stop in a low-k dielectric will illustrate how very different engineering can be from science, and an interesting outlook for students and future engineers who are primarily focusing on science now. The review then continues through the past two decades, highlighting some of the key engineering innovations together with the plasma etch processes that enabled them, including patterning solutions for EUV and multi-layer. Finally, there are the future opportunities of interconnect scaling, arguably even more exciting than the past!

11:40am **PS-ThM-12 Exploring the Use of Tungsten-Based Hard Masks in Beol Interconnects for 3 nm Node and Beyond**, ***Daniel Montero,*** *V. Vega-Gonzalez, H. Puliyalil,* IMEC, Belgium; *J. Nie, J. Yang,* LAM Research; *F. Schleicher,* IMEC, Belgium; *K. Mclaughlin,* LAM Research; *J. Versluijs, F. Lazzarino, S. Park, Z. Tokei,* IMEC, Belgium

Scaling down the average chip size is one of the main drivers in the microelectronics industry, as it broadens the range of applications when smaller, cheaper, more efficient and more powerful chipsets can be installed in tighter packaging. However, scaling down does come with a price, the increased complexity during design and processing. An improvement from the stack composition point of view (materials and thicknesses) is needed, to keep up with the increasing demands while chip downscaling. Novel chip technology nodes require thinner patterning layers, to enable more advanced lithography steps (e.g., EUV lithography), which requires thinner photoresist layers, and therefore, thinner stacks, to transfer the pattern to the dielectric layers underneath [1]. It is in this context when robust and hard to etch materials (Hard Mask materials, HM), with higher etch selectivity are needed.

In the Back End Of Line (BEOL), TiN has been used as the HM of choice from many years in dual damascene applications [2]. As we approach to iN3 nodes and beyond, we face several issues while downscaling. The selectivity during dielectric etch may not be high enough to adequately transfer the pattern (line breaks, increased line roughness, loss of self-alignment during via patterning). TiN layer stress may not be suitable for tighter pitches, which may end up causing line wiggling. Another aspect is that fluorine-based chemistries, used to pattern the dielectrics below the HM, may form TiF salts, eventually leading to possible fail mechanisms.

Tungsten-containing layers have been proposed as viable candidates to replace TiN as HM in more advanced nodes. In this abstract, we first screen different W-containing layers deposited on blanket wafers, with varying W percentage content. Then, we demonstrate the etch development process of three different W-containing layers, acting as HM in line space patterning at tight pitches: at Metal Pitch 36 nm (MP36, line CD 18 nm), by means of an EUV single print lithography process, and at MP21 (line CD 10.5 nm), realized by means of ArFi lithography process and using a self-aligned quadruple patterning (SAQP) exercise. A first trench etch patterning exercise is done on SAQP P21 line space patterns to extract the average line roughness and HM selectivity values.

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12:00pm **PS-ThM-13 Reactive Ion Etch of Subtractive Metal for Advanced Interconnect**, ***Lijuan Zou,*** *Y. Mignot, C. Penny, J. Arnold,* IBM Research Division, Albany, NY; *G. Stojakovic, P. Friddle, S. Schmitz,* Lam Research Corporation

The ability to etch metals in a controlled manner has potential applications at the forefront of advanced interconnect for semiconductor scaling. In this study, the authors evaluate Ru patterning and investigate in depth Reactive Ion Etching (RIE) mechanisms of Ru film in O2/Cl2/CH4 plasma. The etch rate; profile control and mask selectivity of Ru are examined as a function of Cl2/O2 gas ratio; passivation gas CH4 addition and bias power applied. By tuning polymerization, the authors achieve 90º Ru sidewall angle. The impact of various plasma parameters on structural and electrical performance are evaluated using a 300mm Transformer Coupled Plasma (TCP) RIE chamber. The plasma-material interaction is also studied with respect to masking materials. Each of these conditions are evaluated at aggressive critical dimensions to determine the impact of reduced feature size on the ability to anisotropically etch metal structures.

Quantum Information Science Focus Topic
Room 302 - Session QS+AP+EM+MN+NS+SS-ThM

Systems and Devices for Quantum Computing

Moderators: Vivekananda Adiga, IBM, T.J. Watson Research Center, **Kathy-Anne Soderberg**, Air Force Research Laboratory

8:00am **QS+AP+EM+MN+NS+SS-ThM-1 Effects of Environmental Radioactivity on Superconducting Qubits***, L. Cardani, **Ambra Mariani**,* Istituto Nazionale di Fisica Nucleare, Italy **INVITED**

Environmental radioactivity was recently discovered as a potential limit for superconducting quantum bits.

We review recent works proving that ionizing radiation lowers the coherence of singe qubits and induces correlated errors in qubits arrays. We also present preliminary studies showing that operating qubits in a low-radioactivity environment improves their performance. These results fuelled the interest of several European and US groups in further investigating and mitigating radioactivity for next-generation quantum processors.

Using radioactivity measurements and simulations, we estimated the separate contribution of “far” radioactive sources (cosmic rays and laboratory radioactivity) and close materials contamination (chip holder, magnetic shield, …) on a typical chip, focussing on a qubit prototype developed within the SQMS center. We present such contributions and discuss the possibility of mitigating them in "standard" qubit laboratories or, eventually, in deep underground facilities.

8:40am **QS+AP+EM+MN+NS+SS-ThM-3 Dynamics of a Dispersively Coupled Transmon in the Presence of Noise from the Control Line***, **Antti Vaaranta**,* Bluefors Oy, Finland*; M. Cattaneo,* University of Helsinki, Italy*; R. Lake,* Bluefors Oy

In this talk we present theoretical results from a complete description of transmon qubit dynamics in the presence of noise introduced by an impedance-matched resistor (50 Ohm) that is embedded in the qubit control line, acting as a noise source [1]. We derive a model to calculate the qubit decoherence rate due to the noise emanating from this noise source [2]. The resistor is treated, using the Caldeira-Leggett model, as an infinite collection of harmonic LC-oscillators making it a bosonic bath [3]. To obtain the qubit time evolution affected by this remote bath, we start with the microscopic derivation of the Lindblad master equation using the dispersive Jaynes-Cummings Hamiltonian with added inductive coupling to the bath. To solve the resulting master equation, we transform it into a block diagonal form by exploiting its underlying symmetries following Ref. 4. The block diagonalization method reveals that the long time decoherence rate is given by the slowest decaying eigenmode of the Liouvillian superoperator. Moreover, when the readout resonator is in the equilibrium thermal state, the rate of exponential decoherence of the qubit is almost exactly exponential for all times with the predicted rate given by the slowest decaying eigenmode. We also study how the decoherence rate depends on the temperature of the noise source and explore the strong and weak dispersive coupling regimes. The model captures the often used dispersive strong limit approximation of the qubit decoherence rate being linearly proportional to the number of thermal photons in the readout resonator. However, in the dispersive weak limit we predict remarkably better decoherence rates. The model parameters are completely determined by the values of the circuit components, allowing for the exact study of the dynamics on the level of each individual circuit element.

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9:00am **QS+AP+EM+MN+NS+SS-ThM-4 Accurate Microwave Characterization for Superconducting Quantum Technology***, **Slawomir Simbierowicz**,* Bluefors Oy, Finland

Recent breakthroughs in quantum technology have highlighted a need for methods for accurate characterization of cryogenic microwave devices at millikelvin temperatures. In this two-part talk, I will highlight recent progress on microwave measurements at the quantum device reference plane including: (1) system noise characterization of amplifier chains, and (2) calibrated S-parameters of qubit drive line components.In the first part, I will discuss an impedance-matched variable temperature noise source which can be installed in a coaxial line of a cryostat. Using the method of hot/cold source with many input noise temperature points, the system noise temperatures of qubit readout amplifier cascades can be determined. I present measurement results in terms of added noise in Kelvins or photons from a four-wave (4WM) mixing traveling wave parametric amplifier (TWPA) [1], a Josephson parametric amplifier [2], 3WM TWPA, and high electron mobility transistor amplifiers [1].In the second part of the talk, I will present measurements of the 1-port S-parameters of qubit drive line components using a data-based short-open-load calibration at a temperature of 30 mK [3]. The measurement enables us to model systematic errors in qubit state preparation due to non-idealities in qubit control lines such as impedance mismatch. We model the results using a master equation simulation of all XY gates performed on a single qubit. Our work directly addresses the gap between electrical engineering parameters of individual measurement components and performance of the quantum device itself.

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9:20am **QS+AP+EM+MN+NS+SS-ThM-5 Improving Qubit Performance Through Engineering of the Substrate-Josephson Junction Interface***, **Cameron Kopas**, H. Cansizoglu, R. Cochrane, B. Ercan,* Rigetti Computing*; D. Goronzy, C. Torres-Castanedo,* Northwestern University*; J. Oh,* Ames Laboratory*; A. Murthy,* Fermi Lab*; E. Lachman,* Rigetti Computing*; A. Romanenko, A. Grassellino,* Fermi Lab*; M. Kramer, L. Zhou,* Ames Laboratory*; M. Bedzyk,* Northwestern University*; J. Mutus,* Rigetti Computing*; M. Hersam,* Northwestern University*; K. Yadavalli,* Rigetti Computing **INVITED**

The performance of a superconducting qubit is often limited by dissipation and two-level systems (TLS) losses. The dominant sources of these losses are believed to come from interfaces and surfaces, likely as a result of fabrication processes, materials, or atmospheric exposure. We show that certain chemical surface treatments can be used to modify the silicon surface before Josephson junction deposition, reducing the number of strongly-coupled TLS, and improving T1. While identifying specific microscopic sources for loss and TLS is still an open question, targeted characterization of test structures will show which physical changes correlate with performance improvements. We report chemical, structural, and low-temperature microwave characterization of superconducting qubits and films fabricated with different Si surface treatments.

11:00am **QS+AP+EM+MN+NS+SS-ThM-10 Design and Optimal Control of Superconducting Qubits to Achieve Quantum Speed Limits***, **Meenakshi Singh**,* Colorado School of Mines, USA **INVITED**

Fast two-qubit entangling gates are essential for quantum computers with finite coherence times. The finite interaction strength between qubits introduces a theoretical speed limit on the speed of these two-qubit entangling gates. This speed limit has been analytically found only for a two-qubit system under the assumption of negligible single qubit gate times. Here, we demonstrate such a speed limit experimentally using optimal control on two superconducting transmon qubits with a fixed capacitive coupling and finite single qubit gate times. Furthermore, we investigate the effect of additional couplings on the speed limit, both through introduction of an ancillary qubit as well as through utilization of higher transmon energy states. Finally, we discuss the generalization to many qubit systems where properly leveraging all available couplings can provide dramatic speedups.

11:40am **QS+AP+EM+MN+NS+SS-ThM-12 Atomic Scale Processing for Quantum Computing***, **Harm Knoops**,* Oxford Instruments Plasma Technology, Netherlands **INVITED**

With the increasing technological readiness of quantum technology (QT) the field has to start focussing on scalable fabrication methods for quantum bits (qubits) and quantum circuits. This contribution will focus on the enabling role atomic scale processing (ASP) methods such as atomic layer deposition (ALD) and atomic layer etching could play in scaling of QT. The main focus will relate to superconducting qubits and processing of superconducting nanolayers.

Superconducting nanolayers (metals, metal-nitrides) are required for various roles in QT including use in resonators, single-photon detectors, and interconnects.[1] The electrical contacts needed to control the qubits will require non-planar connectivity using superconducting interconnects.[2]Adequate routes for fabrication of planar superconducting layers exist, but for 3D interconnects or through-silicon vias (TSVs), the excellent conformality of ALD nanolayers could be essential. Although for resonators conformality is not a challenge, ALD's thickness control and uniformity should allow high-quality resonators with low spread in properties. For these superconducting nanolayers, metal-nitride compounds have been identified as particularly promising since they exhibit limited surface oxidation (compared to pure metals such as Nb), combined with relatively high critical temperature (T_c) for superconductivity (e.g., as compared to Al). Despite the challenges that the synthesis of high-quality nitrides pose, plasma ALD has demonstrated the capability to deposit high-quality nitrides (e.g., low O content, high electrical conductivity).[3] Furthermore, substrate-biased plasma-ALD offers unique opportunities to obtain and tune high-quality nitrides.[4] For removal of surface oxides or smoothing of resonator surfaces and interfaces, approaches combining ALD and ALE could be of interest.[5] Both ALD and ALE are envisaged to be key tools to allow scaling of these devices and advance the QT field.

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Advanced Surface Engineering Division
Room 317 - Session SE+AS+BI+SS+TF-ThM

Nanostructured and Multifunctional Thin Films and Coatings I

Moderators: Suneel Kodambaka, University of California Los Angeles, **Jianliang Lin**, Southwest Research Institute

8:00am **SE+AS+BI+SS+TF-ThM-1 Nanostructured Optical Thin Films for Energy Applications and More***, **Bill Baloukas,*** Polytechnique Montréal, Canada **INVITED**

The range of applications of optical coatings is ever expanding, and the list of requirements they must fulfil, be it in terms of performance and in terms of functionality, is also increasing. This has stimulated the need for thin film materials with novel nanostructures often based on unconventional materials. The present talk will focus on various coating systems for applications ranging from antireflective (AR) coatings to plasmonic nanocomposites to passive and active materials for anticounterfeiting, smart windows and micro/nanosatellites.

AR coatings are the most widely implemented optical coating solution as they can be found on ophthalmic and camera lenses, displays, solar cells, etc. Most often based on dielectric materials, their mechanical performance can often be problematic when implemented onto polymer substrates, the latter possessing much higher thermal expansion coefficients. As a means of improving their elastoplastic properties, hybrid films consisting of a combination of organic and inorganic materials were explored. We will also show how this concept was pushed further by producing ultralow refractive index hybrid films by glancing angle deposition (GLAD).

GLAD films have also found application in angular selective coatings, which display anisotropic optical properties. Typically based on metals, we show how the angular selectivity (AS) can be tuned independently from the thickness of the film by conformally overcoating dielectric GLAD films with an absorbing film (e.g.: TiN) deposited by atomic layer deposition (ALD).

While the previous examples are based on passive materials, we have also extensively studied active materials, mainly electrochromic (EC) WO_3 and thermochromic (TC) VO_2. We will discuss how by tuning the deposition conditions, one can deposit, for instance, electrochromic interference filters and highly durable EC films when in the presence of significant ion bombardment. In the case of TC VO_2 films, we will show how, by incorporating them into judiciously designed optical filters, one can enhance their overall optical performance (e.g.: luminous transmittance, solar transmission variation, emissivity change, etc.).

Finally, we will conclude this talk by discussing our most recent implementation of a gas aggregation cluster source to produce various nanoparticles of interest for the above-mentioned optical applications.

8:40am **SE+AS+BI+SS+TF-ThM-3 Constitution, Microstructure and Mechanical Properties of Magnetron Sputtered RuAl Thin Films***, **Vincent Ott,*** Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM), Germany*; T. Wojcik,* TU Wien, Austria*; S. Ulrich,* Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM), Germany*; S. Kolozsvári,* Plansee Composite Materials GmbH , Germany*; P. Polcik,* Plansee Composite Materials GmbH, Germany*; P. Mayrhofer, H. Riedl,* TU Wien, Austria*; M. Stueber,* Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM), Germany

Considering high temperature applications, aluminide intermetallics arrived increasing importance over the last decades. They are well known for their mechanical properties, such as high melting point, strength and good oxidation resistance. In Ni-superalloys, for example, aluminide precipitations are widely used as toughening phase, increasing the high temperature strength and durability of the construction material. Although they are commonly used as an additive in composite materials, their usage as a bulk material is hindered by their poor manufacturing due to its brittle behavior at room temperature.

A relatively new candidate material of B2 structured aluminides is the RuAl intermetallic phase. Compared to other candidates of its class, such as NiAl or TiAl, RuAl exhibits a ductile-brittle-transition below room temperature, which may considerably expand the range of its potential applications.

Thin film synthesis can enable the exploitation of their full potential for example as a protective coating in aircraft and aerospace applications. To elucidate this potential, RuAl single layer thin films were synthesized by magnetron sputtering, utilizing a powder manufactured sputtering target with a composition of 50 at. % Ru and 50 at. % Al. Thin film deposition was done for a variation of the process parameters such as the mode of the power supply, gas pressure and substrate bias voltage to investigate their impact on the thin films constitution and microstructure. Major structural thin film characterization was done by X-ray diffraction and transmission electron microscopy methods. These data are subsequently used to discuss the mechanical properties of the thin films, determined by microindentation.

9:00am **SE+AS+BI+SS+TF-ThM-4 Microstructure, Thermal Stability and Oxidation Resistance of an arc-evaporated $Cr_{0.74}Ta_{0.26}N$ Coating***, **Christina Kainz,*** Christian Doppler Laboratory for Advanced Coated Cutting Tools at the Department of Materials Science, Montanuniversität Leoben, Austria*; M. Tkadletz, M. Burtscher,* Department of Materials Science, Montanuniversität Leoben, Austria*; C. Saringer,* Christian Doppler Laboratory for Advanced Coated Cutting Tools at the Department of Materials Science, Montanuniversität Leoben, Austria*; A. Stark, N. Schell,* Institute of Materials Physics, Helmholtz-Zentrum Hereon, Germany*; C. Czettl, M. Pohler,* CERATIZIT Austria GmbH, Austria*; D. Kiener,* Department of Materials Science, Montanuniversität Leoben, Austria*; N. Schalk,* Christian Doppler Laboratory for Advanced Coated Cutting Tools at the Department of Materials Science, Montanuniversität Leoben, Austria

CrTaN coatings have recently received increasing industrial interest due to their combination of high hardness, beneficial fracture toughness and promising performance in cutting tests. However, up to now, no thorough investigation on the thermal stability and oxidation resistance of this coating system is available. Thus, this work aims to elucidate the evolution of the microstructure and phase composition of an arc evaporated $Cr_{0.74}Ta_{0.26}N$ coating in protective atmosphere and air up to 1400 °C. The as–deposited coating crystallizes in an fcc–$Cr_{0.74}Ta_{0.26}N$ solid solution with a preferred <311> orientation. Alternating Cr–enriched and Ta–enriched nano–layers are identified in the cross–section, which arise from the three–fold rotation during deposition. $Cr_{0.74}Ta_{0.26}N$ powder is stable in protective atmosphere up to temperatures of ~1200 °C, where a transformation into fcc-$Cr_{0.74}Ta_{0.26}N$ to t–$Cr_{1.2}Ta_{0.8}N$ sets in. Vacuum annealing of $Cr_{0.74}Ta_{0.26}N$ on sapphire substrate results in the loss of the nano-layers at 1000 °C, a texture change to <200> at 1270 °C and the transformation to t-$Cr_{1.2}Ta_{0.8}N$ at 1300 °C. When exposed to ambient atmosphere, powdered CrTaN starts to oxidize to t–$CrTaO_4$ and r–Cr_2O_3 at 1050 °C. A partly oxidized CrTaN coating on sapphire was found to consist of intact fcc-$Cr_{0.74}Ta_{0.26}N$ grains close to the substrate interface, a porous transition layer of r-Cr_2O_3 and t-$CrTaO_4$ and a dense r-Cr_2O_3 layer at the surface. The present study confirms the exceptional thermal stability and oxidation resistance of CrTaN coatings, making them promising candidates for use in demanding machining applications.

9:20am **SE+AS+BI+SS+TF-ThM-5 Microstructural Characterization and Tribological Evaluation of TiN, CrN, TiSiCN, and CrSiCN Coatings for Applications in Cold Regions***, **Nicholas D'Attilio**, F. Thompson, G. Crawford,* South Dakota School of Mines and Technology*; E. Asenath-Smith,* US Army Corps of Engineers Cold Regions Research and Engineering Laboratory

Transition metal nitride and nanocomposite coatings have the potential to improve the efficiency, service lifetime, and durability of equipment operating in the extremely cold and dry environments found in Earth's polar regions. Ceramic coatings are sensitive to their operating conditions, and development efforts have been focused on ambient and high temperature environments. Thus, there is a need to understand the influence of arctic conditions on the performance of these materials. To investigate the influence of coating phase content on cold environment performance, TiN, CrN, TiSiCN, and CrSiCN coatings were deposited by plasma enhanced reactive magnetron sputtering. The structure and composition of the coatings was characterized by scanning electron microscopy, energy dispersive X-ray spectroscopy, atomic force microscopy, and X-ray diffraction. Tilting base contact angle goniometry was used to determine the surface energy using the Owens-Wendt-Rabel-Kaelble method. Coating hardness and apparent elastic modulus were measured by nanoindentation. Sliding wear tests were conducted under simulated arctic conditions with a ball-on-flat tribometer equipped with an active cooling stage. Coating microstructure, surface properties, and their relationships to the wear mechanisms identified at low temperatures are discussed.

9:40am **SE+AS+BI+SS+TF-ThM-6 Development and Evaluation of TiAlNb/YSZ Protective Coatings for Titanium Alloys***, **Jianliang Lin**,* Southwest Research Institute, San Antonio Texas*; T. Stinnett,* Lockheed Martin Missiles and Fire Control

There are increasing demands in the development of advanced thermal protection coatings for aerospace components made by titanium alloys for hypersonic applications. A conventional thermal barrier coating based on MCrAlY/YSZ produced by thermal spray or EB-PVD (Electron Beam Physical Vapor Deposition) provided thermal protection, but was found insufficient in thermal stain tolerance and mechanical strength match for titanium alloys. In this study, TiAlNb alloy with specific chemistry was selected as the bond coat for Ti-6Al-4V alloys. The TiAlNb bond coats were prepared by different magnetron sputtering techniques, including plasma enhanced magnetron sputtering (PEMS), high power impulse magnetron sputtering (HiPIMS), and a combination of PEMS and HiPIMS. The structure, adhesion, oxidation resistance, and thermal fatigue resistance of the TiAlNb coatings was studied by different means. Then an yttrium stabilized zirconium oxide (YSZ) top coat was applied on the top of the optimized TiAlNb by thermal spray. The thermal strain resistance and phase stability of the overall coating system were evaluated using high energy laser irradiation and compared to a thermal spray MCrAlY/YSZ coating in ambient air. It is found that TiAlNb/YSZ outperform MCrAlY/YSZ in high energy laser irradiation, and exhibited no structure and integrity degradation.

11:00am **SE+AS+BI+SS+TF-ThM-10 Imperfections in Metal Diborides – from Ab-Inito Calculations to Transmission Electron Microscopy***, **Martin Dahlqvist**,* IFM, Linköping University, Sweden*; M. Dahlqvist,* Linköping University, Sweden **INVITED**

Transition metal diborides (MB_2) are considered as an extremely hard ceramics owing to their outstanding chemical, mechanical, corrosion, thermal and electrical properties. This makes MB_2 coatings attractive for applications in erosive, abrasive, corrosive, and high-temperature environments [1]. Typical coatings are overstoichiometric in boron ($B/M>2$) [2] but the recent addition of understoichometic MB_2 coatings ($B/M<2$) have widened their compositional range [3-8]. However, when comparing calculated and measured lattice parameters of MB_2, perfect match is found for *M* from Group 3 (Sc, Y) and 4 (Ti, Zr, Hf) while deviations are found for *M* from Group 5 (V, Nb, Ta) and 6 (Cr, Mo, W). Reason for this have been discussed to be attributed to non-stoichiometric MB_2. In our quest for improving the properties of MB_2 we must thus not only master their composition but also related defects. Reliable theoretical studies thus require detailed information about type of defects and their distribution in MB_2. It will be shown how theory can be used to identify possible defects in MB_2 and explain the discrepancy between theory and experiment. It will be demonstrated that vacancies in MB_2 have a significant impact for *M* from Group 5 (Nb, Ta) and 6 (Mo, W) with improved thermodynamical and dynamical stability as well as mechanical properties. Moreover, extended planar defects have also been identified for multiple MB_2 where atomically resolved aberration-corrected scanning transmission electron microscopy imaging, electron energy loss spectroscopy elemental mapping and first principles calculations have been applied to decode the atomic arrangements of the observed planar defects in non-stoichiometric MB_2 coatings.

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11:40am **SE+AS+BI+SS+TF-ThM-12 Mechanical Property and Corrosion Resistance Evaluation of $Ti_xZrNbTaFeB_y$ High Entropy Alloy Thin Films***, B. Lou,* Chang Gung University, Taiwan*; F. Kan,* Ming Chi University of Technology, Taiwan*; **Jyh-Wei Lee**,* Ming Chi University of Technology, Taiwan

High entropy alloy (HEA) thin films have been widely explored due to their unique properties as compared with conventional alloy coatings. In this work, an equimolar TiZrNbTaFe HEA target and a TiB2 target were used to fabricate five TixZrNbTaFeBy HEA thin films with different Ti and B contents using a hybrid high power impulse magnetron sputtering and radio frequency power deposition system. The Ti and B contents were increased by decreasing the input power of TiZrNbTaFe HEA target. The (Ti+B)/(Zr+Ta+Nb+Fe) ratio of the thin films increased from 2.70 to 19.44 as the ZrTiNbTaFe HEA target input power decreased from 200 to 50 W. The TixZrNbTaFeBy thin film kept its amorphous structure while the (Ti+B)/(Zr+Ta+Nb+Fe) ratio was less than 19.44. A nanocomposite microstructure consisting of TiB_2 nanocrystallites embedded in an amorphous TiZrNbTaFe matrix was obtained for the $Ti_{26.4}Zr_{1.1}Nb_{1.0}Ta_{1.3}Fe_{1.1}B_{61.1}$ thin film. The hardness of TixZrNbTaFeBy thin films increased with increasing Ti and B contents. Good adhesion properties were found for five thin films. Each amorphous TixZrNbTaFeBy thin film enhanced the corrosion resistance of bare 304 stainless steel substrate because of the dense microstructures to block the attack of corrosive electrolytes. The amorphous structured $Ti_{26.9}Zr_{3.5}Nb_{3.4}Ta_{3.8}Fe_{3.7}B_{54.6}$ thin film coating exhibited a potential application as a protective coating in harsh environments due to its high hardness of 18.8 GPa, excellent adhesion, good wear resistance, and adequate anticorrosion property.

12:00pm **SE+AS+BI+SS+TF-ThM-13 Tuning the Properties of Thin Films via Disorder***, **Alessandro Troglia**, M. van de Poll,* Advanced Research Center for Nanolithography (ARCNL), Netherlands*; J. van de Groep, A. de Visser,* Van der Waals-Zeeman Institute, University of Amsterdam, Netherlands*; R. Bliem,* Advanced Research Center for Nanolithography (ARCNL), Netherlands

Structural disorder in thin films is often considered detrimental compared to the well-defined nature of epitaxial layers. However, some examples of amorphous thin films show superior properties such as better corrosion resistance, mechanical strength and catalytic performance. Structural disorder can thus serve as an ideal parameter to tune the properties of thin films to specific applications. In this work, we investigate how structural disorder affects the properties of metallic thin films for two selected alloys: CuZr and HfMoNbTiZr. Due to its excellent glass-forming ability, CuZr is an ideal model system for metallic glasses, while the refractory high-entropy alloy (HEA) HfMoNbTiZr has shown a strong preference towards crystallinity. For both materials, amorphous and crystalline alloy thin films of identical composition were achieved by varying the substrate temperature during deposition onto sapphire substrates via pulsed laser deposition (PLD). Grazing-incidence x-ray diffraction (GI-XRD) demonstrate that CuZr thin films grown at room temperature are fully amorphous, while signs of polycrystallinity are observed at 500°C. The effect of disorder is clearly visible in the optical, transport and corrosion properties. The amorphous films are optically transparent in the visible, while polycrystalline films are dark and reflective. The temperature-dependent electronic transport changes its mode from a bad metal to a chargehopping conductor with an increase in structural disorder. Moreover, the surface chemical properties measured with x-ray photoelectron spectroscopy (XPS) show a clear preference in the surface oxidation of the Cu species. Cu is fully metallic in the disordered film after air-exposure, whereas both oxide and hydroxide species are detected in the polycrystalline film. On the other hand, HfMoNbTiZr thin films grown with PLD are amorphous according to GI-XRD and display a remarkable thermal stability. In contrast with literature, no sign of crystallinity is detected with GI-XRD from room temperature up to 700°C. A further increase of the growth temperature reveals the onset of directed crystallization at 900°C. These results pave the way to the synthesis of metallic thin films with superior and tunable properties via disorder for a wide variety of technological applications.

Surface Science Division
Room 319 - Session SS+AS-ThM

Memorial Session in Honor of Patricia Thiel II

Moderators: James Evans, Ames Laboratory, **Cynthia Jenks**, Oak Ridge Natinal Laboratory

8:20am **SS+AS-ThM-2 Navigating Complex Interfaces: In Memory of Patricia A. Thiel*, Cynthia Jenks,*** Oak Ridge National Laboratory **INVITED**

At a time when simple systems in surface science were the norm, Professor Thiel would choose two paths for her research group. Part of the group focused on the seemingly simplistic and part of the group focused on the seemingly complex. A key to her success was not shying away from complexity or diving deep into the detailed mechanisms of what at first appeared simple, yet turned out to be anything but simple. Additionally, she garnered success by bringing together experts from different disciplines and backgrounds to tackle her research focus areas. Among the areas the group focused on from 1992 through 2008, when I worked with her, was on understanding the deposition of Ag on Ag and also on understanding the vast unknown of quasicrystalline surfaces with their all of their complexity. This talk will highlight some of the research during that time and how that work inspired a move toward understanding more complex interfaces in the field of surface science.

8:40am **SS+AS-ThM-3 Atomic Scale Investigation of Friction Properties of Quasicrystals and Beyond*, Jeong Young Park,*** Korea Advanced Institute of Science and Technology (KAIST) & Institute for Basic Science (IBS), Republic of Korea **INVITED**

Quasicrystals that have rotational symmetry but no translational periodicity has been one of the key topics that Pat Thiel has explored and pioneered. Complex metallic alloys, including quasicrystals and approximants often have peculiar mechanical and tribological properties associated with the unique structure. For example, quasicrystals exhibit high hardness, low friction, and good wear resistance, prompting applications as anti-stick and low friction coatings. In this talk, I highlight the research efforts on nanomechanical and tribological properties of quasicrystal and approximant surfaces using atomic force microscopy. It was found that the friction response on twofold surfaces of the clean Al-Ni-Co decagonal quasicrystal where atoms are arranged periodically along the tenfold axis, and aperiodically in the perpendicular direction was anisotropic at different length scales (macroscale and nanoscale). The result indicates that there is an intrinsic relationship between the aperiodic atomic structure of quasicrystals and their low friction. On the oxidized surface and in the elastic regime, friction is dominated by the bulk properties of the metal beneath the oxide and is not sensitive to whether the metal is quasiperiodic or periodic. I discuss the role of the surface oxide and the length scale of mechanical contact in determining nanomechanical and tribological properties.

In the second part of my talk, I will highlight the recent investigation on the frictional behavior of intercalated water between the hydrophilic surfaces and more hydrophobic two-dimensional atomic layers. The water layers confined between the hydrophilic substrate and hydrophobic layers exhibit the bilayer structure that was proposed by Pat Thiel. We found that the water intercalated between 2-dimensional (2D) materials (e.g., graphene and MoS2) and the hydrophilic substrate increases the friction force between the AFM tip and 2D flakes deposited. Moreover, the friction on both graphene and MoS2 increased as the number of stacking water layers increased. This study provides that the intrinsic vibration modes of the water molecules play a key role in the coupling of the 2D materials modes to the phonon bath of the substrate. Finally, I will address the relationship between nanoscale friction on ultrananocrystalline diamond surface and the surrounding environment of water by using ambient pressure−atomic force microscopy. This result elucidates the role of vapor-phase water in the tribological properties of carbon-based materials.

9:20am **SS+AS-ThM-5 Quantification of Structure-Property Relationships at Interfaces*, Susan Sinnott,*** Pennsylvania State University **INVITED**

Many-body, dynamic charge, physics-based potentials are used in classical molecular dynamics (MD) simulations to investigate the chemistry associated with heterogenous systems. In particular, the interaction of graphene with titanium metal and titanium-carbide-derived-carbon (Ti-CDC) systems are investigated. The resulting Ti-CDC structures are then examined for the adsorption of acid gases. These findings illustrate the usefulness of classical MD simulations in designing new material systems.

9:40am **SS+AS-ThM-6 Metal Nodes in Bimetallic Metal-Organic Frameworks as Isolated Sites for Gas-Phase Catalytic Hydrogenation*, Donna Chen,*** University of South Carolina **INVITED**

The $Cu_xRh_{3-x}(BTC)_2$ catalyst (abbreviated CuRhBTC, BTC^{3-} = benzene tricarboxylate) provides excellent dispersion of active metal sites coupled with well-defined, robust structures for propylene hydrogenation reactions.This material therefore serves as a unique prototype for understanding gas-phase catalytic activity in metal organic frameworks (MOFs). The active sites for hydrogenation are identified as Rh^{2+}, while role of Cu^{2+} is primarily to provide stability for the MOF structure. In situ XRD studies show that the crystalline MOF structure is retained during hydrogenation.The appearance of the O-H stretch for COOH at ~3690 cm^{-1} in the diffuse reflectance infrared Fourier transform spectra is characteristic of defects consisting of missing Rh-O bonds. These experimental results are consistent with the reaction mechanism proposed by density functional theory, in which H_2 is dissociated at a Rh^{2+} site with a missing Rh-O bond, while protonation of the decoordinated carboxylate linker stabilizes the active sites and promotes H_2 dissociation.

11:00am **SS+AS-ThM-10 Quasicrystals in Two Dimensions: From Metals To Molecules And Oxides*, Vincent Fournée,*** Institut Jean Lamour - CNRS-Université de Lorraine, France **INVITED**

Quasiperiodic structures exhibit long-range order like normal crystals but they lack translational symmetry. Quasicrystals were first discovered as a new class of intermetallic compounds, now comprising hundreds of members in binary and ternary systems. They usually adopt either the icosahedral or the decagonal point group symmetry. The discovery of quasicrystals has led to a paradigm shift in crystallography and has attracted a large interest in the material science community, motivated by unexpected physical properties that could be linked to quasiperiodicity. This remarkable class of materials has also challenged our understanding of metal surfaces. An atomic scale description of their surfaces is especially important, as it forms the basis for understanding and predicting phenomena such as gas adsorption, metal epitaxy, and friction. Pat Thiel and her group played a major role in the surface science of quasicrystals.

Pat Thiel also pioneered studies of nucleation and growth of metal thin films on quasicrystalline surfaces, demonstrating that local pseudomorphic growth can occur due to preferred adsorption of the metal ad-species at specific sites of the surface quasilattice. The idea was that the complex potential energy surface of quasicrystalline surfaces could serve as a template to grow new 2D quasicrystalline systems.

Here, we will review the different results obtained along this direction, from local peudomorphic growth of Al starfish islands on the 5-fold surface of the icosahedral *i*-Al-Cu-Fe quasicrystal [1] to pseudomorphic single layer high islands in the case of Ag/5f-Al-Pd-Mn [2] and up to the formation of complete 2D quasiperiodic metal layers (Pb, Bi or Sn) templated on various quasicrystalline surfaces [3]. Self-organized molecular films with long-range quasiperiodic order could also been grown by using the complex potential energy landscape of quasicrystalline surfaces as templates. The long-range order arises from a specific subset of quasilattice sites acting as preferred adsorption sites for the molecules, thus enforcing a quasiperiodic structure in the film [4]. Finally we will show some recent examples of 2D quasicrystalline oxide layers obtained by reduction of ABO_3 perovskite thin films grown on Pt(111) [5,6].

[1] T.A. Cai *et al.*, Surface Science, 526 (2003) 115-120.

[2] B. Unal *et al.*, Phys. Rev. Lett., 102 (2009) 196103.

[3] J. Ledieu *et al.*, PRB Rapid Comm., 77 (2008) 073409.

[5] V. Fournée *et al.*, ACS Nano, 8 (2014) 3646–3653.

[6] S. Förster *et al.*, Nature, 502 (2013) 215–218.

[7] C. Ruano M. *et al.*, Phyc. Chem. Chem. Phys., 24 (2022) 7253.

11:40am **SS+AS-ThM-12 Unusual Flat and Extended Morphology of Intercalated Cu Under MoS_2, *Dapeng Jing*,** *Y. Han, J. Evans, M. Kolmer, Z. Fei, M. Tringides,* Ames Laboratory USDOE **INVITED**

There has been intensive research on ultra-thin metal films and surface structures for use as transparent conductor layers in optical and thermal applications. In this study, we present a novel approach to fabricate such metal structures of Cu encapsulated near the surface of a layered material, MoS_2. We use scanning electron microscopy, atomic force microscopy and x-ray photoelectron spectroscopy to characterize this Cu-MoS_2 system formed via physical vapor deposition of Cu in ultrahigh vacuum at 1000 K. Necessary conditions for encapsulation are preexisting ion-induced defects in the MoS_2 substrate and elevated deposition temperature of 1000 K. Under such conditions, Cu grows both on the MoS_2 surface as facetted clusters and beneath the MoS_2 surface as encapsulated structures. The encapsulated Cu starts underneath a surface cluster and grow laterally in size maintaining a thickness of under 10 nm. The Cu structure growth behavior deviates significantly from the Cu intercalation in graphite system where Cu predominantly grows as intercalated islands with much smaller lateral size. Density functional theory calculations reveal the driving force for Cu mass transport from surface clusters to encapsulated structures.

12:00pm **SS+AS-ThM-13 Helium Ion Microscopy for Surface Modification and Characterization, *Alex Belianinov,*** Sandia National Laboratory **INVITED**

There is a growing need to expand the experimental arsenal with tools to visualize and modify materials at a breadth of scales, from atomic to visible with a naked eye. The helium ion microscope (HIM) offers a large dynamic range, and quickly gained popularity since its debut in 2006. Its unique gas field ion source (GFIS) is ideal for high-resolution imaging, milling, localized damage, direct-write, and additional analytical techniques like secondary ion mass spectrometry as well as ion beam induced current imaging.

This presentation aims at providing an overview of the status of HIM technology for imaging, analysis, and nanofabrication. Specifically, the instrument design, ion-matter interaction, imaging, localized material modification, and material characterization will be discussed. Contrast will be drawn between the HIM and other focused ion beam tools in this class that rely on liquid metal alloy ion sources. Current challenges and research opportunities for ion beam tools will be highlighted. A plethora of supporting examples of working with 2D, cleanroom-relevant, soft, polymeric, and biological materials will be shown.

This presentation is dedicated to my mentor and advisor Prof. Patricia A. Thiel. She lives on through the memories of all of us that were lucky enough to spend time with her.

Acknowledgement

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Thin Films Division
Room 316 - Session TF+AP-ThM

Novel ALD CVD Precursors, Processes, Deposited Morphologies and Substrate Architectures

Moderators: Parag Banerjee, University of Central Florida, **Richard Vanfleet**, Brigham Young University

11:00am **TF+AP-ThM-10 The Electrical and Magnetic Properties of Nonstoichiometric Nickel Oxide Thin Films, *Mari Napari,*** University of Southampton, UK **INVITED**

Nonstoichiometric nickel oxide (NiO_x), a p-type oxide semiconductor, has gained significant attention due to its versatile and tunable properties. It has become one of the critical materials in wide range of electronics applications and highly sensitive and selective sensors. In addition, the wide band gap and high work function, coupled with the low electron affinity, have made NiO_x widely used in emerging optoelectronics and p-n heterojunctions [1,2]. Also, it is a commonly applied material in heterogenous catalysis. The properties of NiO_x thin films depend strongly on the deposition method and conditions. Efficient implementation of NiO_x in next-generation devices will require controllable growth and processing methods that can tailor the physical, electronic, and magnetic properties of the material.

In this presentation I discuss our work that links together the fundamental electronic properties of NiO_x thin films with the chemical processing methods, and how these can be used in device applications. I discuss how the p-type nature of NiO_x arises and how its stoichiometry affects its electronic properties, and present results that show how the antiferromagnetic nature of the NiO prevails also in the non-stoichiometric films. I will present examples of NiO_x thin films grown by the chemical deposition techniques, including CVD, ALD, and solution processing approaches, and show how these films can successfully be used in a range of devices and applications, including perovskite solar cells and photoelectrocatalysis [3,4].

[1] Napari et al. "Antiferromagnetism and p-type conductivity of nonstoichiometric nickel oxide thin films" InfoMat 2 (2020) 769-774

[2] Napari et al. "Nickel oxide thin films grown by chemical deposition techniques: Potential and challenges in next-generation rigid and flexible device applications" InfoMat 3 (2021) 536-576

[3] Zhao et al. "In Situ Atmospheric Deposition of Ultrasmooth Nickel Oxide for Efficient Perovskite Solar Cells" ACS Appl. Mater. Interfaces 10 (2018) 41849-41854

[4] Innocent et al. "Atomic scale surface modification of TiO_2 3D nano-arrays: plasma enhanced atomic layer deposition of NiO for photocatalysis" Mater. Adv. 2 (2021) 273-279

11:40am **TF+AP-ThM-12 Al_2O_3 Thin Films with Controlled Nanoporosity Prepared by Low Temperature Thermal ALD, *Marceline Bonvalot*,** *S. Hekking,* LTM - MINATEC - CEA/LETI, France*; C. Vallée,* SUNY POLY, Albany

Because Al_2O_3 is a cheap and abundant material with a very high hardness and inertness to numerous chemicals, porous alumina thin films find a great variety of applications as a filtering material of liquids in the food industry, oil and gas industry, pharmaceutical industry and in biotechnologies as well. In this work, we describe an original experimental route, which leads to the production of Al_2O_3 thin films with controlled nanoporosity. The deposition is carried out by thermal ALD with trimethyl aluminum (TMA) as precursor and at low temperatures (between 50°C and 80°C). The process temperature is deliberately set below the precursor temperature window, so that a significant amount of carbon-rich contaminants remain in the produced thin film, due to poor decomposition of the precursor at low thermal energy. An intermediate O_2 plasma step is then inserted within the thermal ALD cycles, which helps for the degassing of these contaminants leaving behind nanoscale porosities within the thin film under growth. The process optimisation will be presented by discussing the impact of incident plasma power and duration on carbon-rich contamination levels. The frequency of the occurence of the O_2 plasma step inserted within the thermal ALD process will also be investigated, and discussed in regards to imperfectly perfect materials strategies.

12:00pm **TF+AP-ThM-13 Thermal ALD Process of NiO Based on $Ni(^tBu\text{-}MeAMD)_2$ Precursor, *Cristian van Helvoirt*,** *N. Phung, M. Creatore,* Eindhoven University of Technology, Netherlands

The applications of NiO thin films have increased over the last years, especially in the fields of electrocatalysis for water-splitting [1] and metal halide perovskite photovoltaics [2]. Previously, we reported an ALD-process for NiO based on bis-methylcyclopentadienyl-nickel as precursor and O_2-plasma as the co-reactant [3]. In this contribution, we investigate a thermal ALD process of NiO, with the motivation of expanding the ALD process capabilities on sensitive (e.g. to O_2 plasma) hybrid organic-inorganic chemistry substrates and offering opportunity for NiO process upscaling by spatial ALD, which is generally based on thermal processes.

For the present study, we selected (N,N′-di-tert-butylacetamidinato)Nickel(II) ($Ni(^tBu\text{-}MeAMD)_2$) based on the relatively low melting point (87°C) with reasonable vapor pressure, and the availability of the precursor. Although literature addresses several thermal ALD processes of NiO based on $Ni(^tBu\text{-}MeAMD)_2$ with reasonable growth rates [4,5], to our best knowledge, no saturation curves have been reported and only hot wall reactors were used so far. The decomposition temperature of the precursor (237°C), can limit the processing temperature, thereby suggesting the application of cold wall reactors. Hence, in this study, we use a cold wall reactor (FlexAL^{TM} MK1 Oxford Instruments).

We report saturation curves using $Ni(^tBu\text{-}MeAMD)_2$ as the precursor and H_2O as the co-reactant resulting in a growth per cycle of 0.40-0.80 Å within a temperature window of 50-200°C. The process at ALD saturated condition also yields excellent uniformity (≥92% homogeneity over an 8 inch silicon wafer), with low impurity level in the film (3% C and 1% N), as observed by X-ray photoelectron spectroscopy (XPS). Rutherford backscattering spectroscopy analysis confirms a nearly stoichiometric film of O:Ni = 1.1 (deposition at 150°C). XPS also reveals the presence of oxide and (oxy)hydroxide terminal groups indicating the presence of both Ni^{2+} and Ni^{3+} oxidation states, imparting the p-type character to the film, key for selective hole transport behavior. Moreover, X-Ray diffraction data show a preferred orientation in the (111) direction for the film as opposed to (200) earlier observed in plasma-assisted ALD NiO, and beneficial for the O_2 evolution reaction in water-splitting [1].

57. Chen, *et al.* (2019) *Chem. Eur. J. 25*, 703 – 713
58. Phung, *et al.* (2022) *ACS Appl. Mater. Interfaces 14*, 1, 2166–2176
59. Koushik, *et al.* (2019) *J. Mater. Chem. C7*, 12532–12543
60. Thimsen, *et al.* (2012) *J. Phys. Chem. 116,* 16830–16840
61. Hsu, *et al.* (2015) *Nanotechnology26*(38), 385201

Thin Films Division
Room 316 - Session TF1+SE+SS-ThM

Nucleation, and Interface Phenomena in Thin Films

Moderators: Adrie Mackus, Eindhoven University, Netherlands, **Qing Peng**, University of Alabama

8:00am **TF1+SE+SS-ThM-1 Opportunities of Complex Oxides Prepared by Atomic Layer Depositions***, P. Sallés, P. Machado,* ***Mariona Coll***, ICMAB-CSIC, Spain **INVITED**

The rapid development of electronic devices, telecommunication systems, and sensors pushes new functional demands with increasingly stringent requirements like flexibility, light weight, and miniaturization. Transition metal oxides present the richest variety of functional properties due to the large diversity of chemical compositions and structures that they can offer. However, the preparation and manipulation of crystalline yet bendable functional complex oxide membranes has been a long-standing issue as they require specific crystalline substrates and high temperature treatments. We have developed a facile chemical route based on the use of $Sr_3Al_2O_6$(SAO) sacrificial layer to detach oxide thin films of various compositions from the growing substrate and enable their transfer to flexible substrates.[1] Meticulous chemical and structural study of the SAO film have allowed us to identify the formation of an amorphous SAO capping layer and carbonates upon air exposure, which dictate the crystalline quality of the subsequent oxide film growth.[2] Judicious cation substitution in SAO enabled both decreasing reactivity with ambient moisture and modulating the strain state of the subsequent heterostructures grown on it. Upon detailed investigation of oxide adhesion on polymeric substrates and sacrificial etching (figure 1), crystallinity, surface morphology, interface cation diffusion, mechanical and electrical properties of transfer printed heteroepitaxial $BiFeO_3/La_{0.7}Sr_{0.3}MnO_3$ membranes have been studied and compared with rigid substrates. From this work it is envisaged many new opportunities to prepare artificial oxide heterostructures and devices offering a whole new dimension for electronics and beyond.

[1] P. Salles, M. Coll et al. Adv. Funct. Interfaces, 2001643 (2021)

[2] P. Salles, M. Coll et al. ACS Appl. Mater. Interfaces , 14, 10, 12845–12854 (2022)

8:40am **TF1+SE+SS-ThM-3 An Atomic-Scale Study of Si Epitaxial Growth on Cl-Si(100)***,* ***Azadeh Farzaneh,*** University of Maryland, College Park*; R. Butera,* Laboratory for Physical Sciences

Atomically-precise fabrication techniques utilize a scanning tunneling microscope to lithographically define electronic devices and components, where a monatomic layer of H or Cl adsorbed on Si(100) acts as a resist. Unlike traditional resists, these monatomic resists either desorb or remain at the growth front during subsequent growth of Si capping layers.While the body of literature extensively explores Si deposition and subsequent diffusion on H-Si(100), Cl-Si(100) has remained relatively unexplored.A detailed understanding of the thin film growth mechanism enables atomic level control of the interface, which starts with diffusion of adatoms in dilute regimes on the surface. Here we explored the initial stages of Si growth on Cl-Si(100) and characterized thin Si films (~25 nm) grown on this surface. The activation energy for Si adatom diffusion on Cl-Si(100) was extracted from STM observations combined with simulations of a simple random walk model rooted in the mechanism of Si chain formation at different temperatures. Ex-situ characterization of thin Si films grown on Cl-Si confirmed the formation of crystalline layers and the near complete removal of Cl from the Si matrix. The epitaxial film obtained on Cl-Si(100) and absence of Cl from the interface confirm Cl as a viable resist for current atomically precise fabrication schemes. This opens up new pathways for introducing new chemistries and materials into the picture.

9:00am **TF1+SE+SS-ThM-4 The Effect of Oxygen Plasma on the ZnO Growth on Polymer Substrates During Plasma-Enhanced Atomic Layer Deposition***,* ***Lisanne Demelius,*** Graz University of Technology, Austria*; M. Blatnik,* CEITEC – Central European Institute of Technology, Brno University of Technology, Czechia*; K. Unger,* Graz University of Technology, Austria*; P. Parlanti, M. Gemmi,* Istituto Italiano di Tecnologia, Center for Materials Interfaces, Italy*; A. Coclite,* Graz University of Technology, Austria

Atomic layer deposition (ALD) is a powerful technique to deposit highly conformal thin films the thickness of which can be precisely controlled. However, the use of polymeric substrates often leads to non-ideal ALD processes that result in precursor diffusion and subsurface growth of the deposited material.
Plasma-enhanced ALD (PE-ALD) is known to enhance nucleation due to the surface-activating effect of plasma and can be expected to significantly reduce subsurface diffusion, enabling the surface-limited deposition of thin conformal coatings. However, plasma can also have detrimental effects on polymeric substrates.

Our work contributes to a deeper understanding of how oxygen plasma applied during PE-ALD affects film formation, nucleation, and interface formation of ZnO on polymer substrates. In-situ spectroscopic ellipsometry was used as the main technique to monitor the PE-ALD growth of ZnO on selected polymer thin films. To better understand how the chemical structure of the polymer influences plasma-substrate interactions and ZnO thin film formation, both crosslinked and linear polymers exhibiting varying degrees of reactivity with the ALD precursor were studied.

Our results show that while the plasma efficiently activates the polymer surface to enable rapid ZnO nucleation, it can also cause significant substrate etching that dominates the initial stage of growth until, at a certain point, ZnO growth takes over and the regime of normal ALD growth behavior is entered. The strength and extent of etching strongly depends on the type of polymer. Despite the initial etching, the resulting thin films exhibit sharp interfaces and a quality, in terms of surface roughness, crystallinity and ZnO density, comparable to those of ZnO deposited on silicon.

A closer examination of the first 25 PE-ALD cycles showed that, on the nanometer scale, the simultaneous etching of the polymer and ZnO nucleation leads to a certain degree of intermixing at the interfaces, the extent of which depends on the type of polymer. It was also revealed that, during the first few cycles, no stochiometric ZnO is yet formed but instead Zinc is found to be bonded to hydroxyl groups and presumably oxygen-carbon species from the polymer, forming hybrid bonds. This points to a strong interaction between the polymer substrate and the forming ZnO, which can be expected to result in good film adhesion, a property that is critical in all applications involving mechanical stress and strain.

9:20am **TF1+SE+SS-ThM-5 Measuring Local Atomic Structure Variations Through the Depth of Ultrathin ALD Aluminum Oxide***,* ***Nikhila Paranamana,*** *M. Young, R. Gettler, H. Koenig, S. Montgomery-Smith, X. He,* University of Missouri, Columbia

Understanding the atomic structure of ultrathin (<20 nm) atomic layer deposition (ALD) coatings is critical to establish structure property relationships and accelerate the application of ALD films to address technological needs. Previous studies have measured the atomic structure of nanoscale ALD films using cryogenic electron diffraction with a large (~200 nm) beam diameter. However, for ultrathin ALD coatings, these measurements provide only ensemble average structural information and cannot be used to directly measure differences in atomic structure through the depth of the ALD film. In this study, we localize the electron beam to a small (~ 5 nm) spot size using cryogenic scanning transmission electron microscope (STEM) and we collect electron diffraction data at multiple points along the depth of a 12 nm thick ALD AlO_x film deposited onto a CNT substrate without a contribution from the substrate. We couple these diffraction measurements with pair distribution function (PDF) analysis and iterative reverse Monte Carlo-molecular statics (RMC-MS) modeling to compare atomic structure metrics at different positions in the film depth. We interpret the modeling results considering the 3D concentric cylindrical sample geometry of a CNT with uniform AlO_x coating. These measurements confirm a two-phase bulk/interface structural model proposed previously for ALD AlO_x, and indicate that the interfacial layer at the CNT-AlO_x interface is 2.5 nm thick – five times larger than previously reported. This report demonstrates direct measurement of atomic structural variations across ultrathin films that is of broad interest for understanding local differences in atomic structure across material interfaces.

9:40am **TF1+SE+SS-ThM-6 Interfacial Reactions and Energy Transfer in Sputter Deposited Thermite Reactive Nanolaminates***, **Chloe Skidmore**, J. Maria,* Pennsylvania State University

Cost effective energetic materials with highly tunable ignition and actuation have important applications in both military and commercial sectors. Recently, interest has grown in nanoenergetic composites due to their potential as stand-alone explosives with greater reliability, heat release, and combustion efficiency. Thermite is a versatile inorganic energetic of specific significance due to the highly exothermic reduction-oxidation reaction that occurs between metal and oxide constituents, resulting in self-sustaining heat production. However, if the high energy release and improved tunability provided by the diverse chemistries of inorganic energetics is to be utilized, a fundamental understanding of the initiation and propagation processes in new nanoenergetic materials such as thermite is necessary. Thin film deposition of multilayered stacks of alternating metallic and oxide layers with well defined interfaces offers a streamlined process to observe energy transduction and the chemical reactions that mitigate interface reactions. These multilayered stacks, termed reactive nanolaminates (RNLs), facilitate control over reactant thickness, diffusion distance, interface quality and the total material involved, while also reducing premature intermixing of metal and oxide layers. This presentation explores energy release in sputter deposited CuO-Mg RNLs as a function of bilayer thickness, plasma energetics, and metal-oxide layering sequence. These samples are analyzed via in-situ high temperature x-ray diffraction (XRD) and differential scanning calorimetry (DSC), as both probe the oxygen exchange process by structure evolution and energy production, respectively. The bulk properties associated with the Mg-CuO thermite system suggests extensive oxygen dissolution in the starting metal and the possibility of transient eutectic liquid formation during reaction. XRD results indicate that CuO/Mg RNLs exhibit eutectic liquid formation during reaction, with Cu_xMg_yintermetallics temporarily appearing around 565°C. DSC analysis reveals exotherm maxima at temperatures associated with critical points in the Mg-Cu phase diagram. More precisely, as interfacial area is increased the max exothermic peak shifts from ~650°C (T_m Mg) to ~565°C (T_m Mg_2Cu) before finally occurring at ~483°C (T_m eutectic Mg/Mg_2Cu). Preliminary DSC analysis also suggests that, relatively speaking, sputtering energetics resulting in smoother, more crystalline Mg interlayers, shifts the maximum exothermic peak to higher temperatures. These findings provide insight into the mechanisms of energy transfer in thermite RNLs, allowing for highly tunable, reliable energetic materials.

2D Materials Technical Group

Room 303 - Session 2D+AS+EM-ThA

2D Materials: Electron Microscopy and Photoemission Spectroscopy

Moderators: Keun Su Kim, Yonsei University, Republic of Korea, **Dmitry Kireev**, University of Texas at Austin

2:20pm **2D+AS+EM-ThA-1 Periodic Lattice Displacements in Low Dimensional Materials***, **Robert Hovden,*** University of Michigan **INVITED**

Dramatic electronic changes are associated with periodic lattice displacements [1] where structure, even in 2D materials, requires higher dimensional measurement using scanning / transmission electron microscopy. In particular charge density waves are an emergent periodic modulation of the electron density that permeates a crystal with strong electron-lattice coupling. Strong evidence suggests that transformative correlated electron behavior may exist only in unrealized clean 2D materials such as 1T-TaS$_2$. Unfortunately, experiment and theory suggest that extrinsic disorder in free standing 2D layers impedes correlation-driven quantum behavior. Here we demonstrate a new route to realizing fragile 2D quantum states through epitaxial polytype engineering of van der Waals materials. The isolation of truly 2D charge density waves (CDWs) between metallic layers stabilizes commensurate long-range order and lifts the coupling between neighboring CDW layers to restore mirror symmetries via interlayer CDW twinning. The twinned-commensurate (tC-) CDW reported herein has a single metal–insulator phase transition at ~350 K as measured structurally and electronically [2]. Fast in-situ transmission electron microscopy and scanned nanobeam diffraction map the formation of tC-CDWs. This work introduces epitaxial polytype engineering of van der Waals materials to access latent 2D ground states distinct from conventional 2D fabrication.

Here we show the critical temperature for spatially-coherent, commensurate (C-) CDW in 1T-TaS$_2$ can be raised to well above room temperature (~150 K above the expected transition) by synthesizing clean interleaved 2D polytypic heterostructures. This stabilizes a collective insulating ground state (i.e. C-CDW) not expected to exist at room temperature. We show the formation of these spatially coherent states occurs when 2D CDWs are confined between metallic prismatic polytypes. At the same time, interleaving disables interlayer coupling between CDWs. This raises the critical temperature of the C-CDW and forms out-of-plane twinned commensurate (tC) CDWs as revealed by scanned nanobeam electron diffraction. These results demonstrate polytype engineering as a route to isolating 2D collective quantum states in a well-defined extrinsic environment with identical chemistry but distinct band structure.

[1] *Nature and evolution of incommensurate charge order in manganites visualized with cryogenic STEM,* I. El Baggari et al. **Proc. Natl. Acad. Sci. U.S.A. 115**, 1445 (2018)

[2] *Two-dimensional charge order stabilized in clean polytype heterostructures*, S. H. Sung et al. **Nature Communications**, **13** 413 (2022)

3:00pm **2D+AS+EM-ThA-3 Engineering of Nanoscale Heterogenous Transition Metal Dichalcogenide-Au Interfaces***, **Alex Boehm,*** Sandia National Laboratories*; J. Fonseca,* Naval Research Laboratory*; K. Thuermer, J. Sugar,* Sandia National Laboratories*; J. Robinson,* Naval Research Laboratory*; T. Ohta,* Sandia National Laboratories

2-D transition metal dichalcogenides (TMDs) have recently garnered much attention owing to their extraordinary physical, chemical, electrical, and optical properties. However, early material and device studies have revealed that these properties can be greatly impacted by extrinsic factors such as substrate interactions, mechanical strain, and charge transfer. Thus, a careful understanding of the nuanced interactions between TMDs and other materials is critical for high performance devices. Of particular importance are the interfaces with metallic contacts. Here, one barrier are the spatial nonuniformities recently reported at these types of interfaces. Uncovering the impact of these heterogeneities on TMD properties and establishing strategies to control TMD-metal interfaces could enable an array of engineering pathways for future applications. In this work, we find that the electronic structures of mechanically exfoliated TMD-Au interfaces exhibit pronounced heterogeneity arising from microstructure of the supporting metal. Pertinent for device applications these electronic structure variations indicate fluctuating doping levels and Schottky barrier height across the junction. We examined the electronic structures of WS2 and WSe2 at high spatial resolution via photoemission electron microscopy (PEEM) revealing key differences in work function and binding energies of the occupied states. Furthermore, the inherent role of the underlying Au microstructure on the TMD electronic structure is revealed by electron backscatter diffraction (EBSD) and scanning tunneling microscopy (STM). Finally, simple processing methods are employed to fabricate homogenous TMD-Au interfaces while also tuning the electronic properties of the TMDs. Our findings illustrate that the electronic properties of TMDs are greatly impacted by metal interface interaction and provide a means to engineer these important junctions.

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3:20pm **2D+AS+EM-ThA-4 Advanced Laboratory-Based Momentum Microscopy and PEEM Analysis***, **Stefan Böttcher Böttcher,*** SPECS Surface Nano Analysis GmbH, Germany*; D. Singh, T. Conard,* IMEC, Belgium*; M. Wietstruck,* SPECS Surface Nano Analysis GmbH, Germany*; P. van der Heide,* IMEC, Belgium*; A. Thissen,* SPECS Surface Nano Analysis GmbH, Belgium

Momentum Microscopy is a new technology for comprehensive surface analysis, providing high energy and angular resolved band structure mapping combined with advanced surface imaging capability. Extending this technology with laboratory-based instrumentation opens the possibility for detailed studies of new materials under well controlled environments. The combination of a PEEM lens for surface microscopy and momentum microscopy, allows for small spot analysis in ARPES and chemical sensitive surface mapping. In a joint project between IMEC and SPECS the possibilities for laboratory-based momentum microscopy, laser ARPES and x-ray spectroscopy and microscopy are evaluated in the framework of semi-industrial environment. We present a status report at the intersection between fundamental and applied research in surface science. We focus on the use of ARPES characterization in novel materials close to applied research and the functionality of x-ray analysis in PEEM and spectroscopy for chemical analysis.

3:40pm **2D+AS+EM-ThA-5 Epitaxial Growth and Electronic States of Ultrathin Bi (111) Films on Insb (111)B: Evidence of Inversion Symmetry Breaking via Film-Substrate Interactions***, **Hadass S. Inbar**, J. Dong, A. Engel, C. Dempsey, Y. Chang,* University of California Santa Barbara*; A. Fedorov,* Advanced Light Source, Lawrence Berkeley National Laboratory*; C. Palmstrom,* University of California Santa Barbara

Quantum size effects in bismuth films have been the focus of the scientific community for decades. The spin–split Rashba surface states and large mass anisotropy in surface state valleys have made Bi films a promising system for future applications in spintronics and valleytronics. Moreover, in the field of topological materials, the Bi (111) bilayer (BL) is predicted to behave as a quantum Hall spin insulator[1]. Along the Bi (111) step edges, 1D helical modes were observed[2], an ingredient in one proposed platform to construct Majorana zero modes[3]. However, the synthesis of continuous ultrathin (<6 BL) Bi (111) epitaxial films on semiconducting substrates has remained a materials challenge. We report a study of ultrathin large-area Bi (111) layers grown on InSb (111)B substrates by molecular beam epitaxy and in-vacuo transferred for scanning tunneling microscopy and synchrotron-based angle-resolved photoemission spectroscopy. We show that large-area single-domain ultrathin Bi films can be stabilized through strong film-substrate interactions. Our study follows the evolution of tensile strain in the films, which is predicted to lead to a semimetallic to semiconducting transition. With decreasing film thickness from 13 to 1 BL, we quantify the confinement-induced shifts in the bulk band structure and trace the quantum well energy levels with a phase shift accumulation model. Significant substrate-film interactions breaking inversion symmetry affect the surface state dispersion leading to a surface state degeneracy which allows us to assign the topological order in Bi(111) thin films. The findings of this study offer a new route for epitaxial growth and integration of band-engineered Bi films with III-V substrates.

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[2] Drozdov, I. K., Alexandradinata, A., Jeon, S., Nadj-Perge, S., Ji, H., Cava, R. J., ... & Yazdani, A. (2014). One-dimensional topological edge states of bismuth bilayers. Nature Physics, 10(9), 664-669.

[3] Jäck, B., Xie, Y., Li, J., Jeon, S., Bernevig, B. A., & Yazdani, A. (2019). Observation of a Majorana zero mode in a topologically protected edge channel. Science, 364(6447), 1255-1259.

4:00pm **2D+AS+EM-ThA-6 Band Modulations: Revealing Moiré Effects in Twisted Bilayer 2D Materials***, **Ryan Muzzio**,* Carnegie Mellon University*; A. Jones, P. Majchrzak,* Aarhus University, Denmark*; H. Martins, S. Singh,* Carnegie Mellon University*; C. Jozwiak, A. Bostwick, E. Rotenberg,* Lawrence Berkeley National Laboratory*; P. Hofmann,* Aarhus University, Denmark*; S. Ulstrup,* aarhus University, Denmark*; J. Katoch,* Carnegie Mellon University

Two dimensional (2D) materials are a wonderful template to explore novel quantum phenomena in the ultra thin limit.They can be exfoliated to the desired thickness, stacked with other 2D flakes, and be integrated in device fabrication for electrical measurement.The addition of a twist angle between stacked 2D flakes produces a moiré lattice which can lead to drastic changes in their physical properties.For the case of bilayer graphene, introducing a ~1.1 degree rotation (the magic angle) leads to a low temperature superconducting state[1].This remarkable transport result has been explained via band structure theory and experiment[2,3,4] of the hybridization of the out-of-plane Pi orbitals of the graphene layers which forma weakly dispersing state at the fermi level.Beyond graphene, twist-angle dependent bilayer transition metal dichalcogenides (TMDCs) also display extraordinary novel moiré physics[5,6].In this presentation, we will discuss our ongoing analysis of nano- and micro-focused angle resolved photoemission spectroscopy (ARPES) performed on twisted bilayer graphene and TMDCs systems placed on hBN.We demonstrate, over a wide range of twist angles, the effect of the moiré lattice and proximity effects on the band structure by investigating the effective masses, band positionings, and location of the moiré bands across four TMDC heterobilayers.Our work demonstrates the tunability of the electronic properties in twisted 2D bilayers and the power of ARPES to provide a momentum-resolved view of their electronic structure.

Applied Surface Science Division
Room 320 - Session AS+2D+EM+MS+NS+SS+TF-ThA

Probing Defects at Surfaces and Interfaces

Moderators: Michaeleen Pacholski, The Dow Chemical Company, **Zachary Robinson**, SUNY Brockport

2:20pm **AS+2D+EM+MS+NS+SS+TF-ThA-1 Controlling InP Quantum Dot Surface Defects Using ALD-inspired Surface Chemistry and Phosphorus Kα and Kβ X-ray Emission Spectroscopy***, **Nayon Park**,* University of Washington **INVITED**

Colloidal InP quantum dots are a leading heavy-metal-free semiconductor material for spectral downconversion in current generation display technologies and future generation energy efficient LEDs. Achieving the brightest and narrowest photoluminescence (PL) relies on the synthesis of structurally and electronically defect-free quantum dots. InP quantum dots' high propensity for oxidation and the inherent oxidative defects arising from commonly used synthesis methods therefore motivates a systematic approach to probe InP oxidation as a function of synthesis and surface treatments and correlation with the resultant optical properties. Phosphorus X-ray Emission Spectroscopy (XES) presents itself as an exceptional tool in this regard. In this talk, I will show recent results from computational modeling where we find that native InP surface oxides give rise to dark states near the band edge. Replacing the surface indium with zinc to form a monolayer ZnO shell results in the reduction of dark states. Using ALD-inspired successive ionic layer adsorption and reaction (SILAR), we developed the colloidal, layer-by-layer growth strategy of metal oxide shells (i.e. ZnO, CdO, GaO_x, AlO_x) on InP quantum dots at room temperature using common ALD precursors (*i.e.*, metal alkyls and water). Metal oxide-shelled InP QDs generally show enhanced PL and evidence of bulk and local structural perturbations arising from the metal oxide as determined by X-ray diffraction and X-ray absorption spectroscopy. Further, we explore the impact of these metal oxide interfaces on the PL QY and emission linewidth of InP/ZnSe core/shell QDs. Upon growing a thin ZnSe shell, we observe improved PL properties, which we hypothesize to be attributable to the inhibition of phosphorus migration to the shell due to the presence of the metal oxide interlayer, as supported by X-ray emission spectroscopy. Taken together, these results suggest a clear path forward in the control and design of complex QD interfaces with atomistic insight for optoelectronic technologies.

3:00pm **AS+2D+EM+MS+NS+SS+TF-ThA-3 Characterization of MAX Phases using a Combination of Micro-spot XPS, HAXPES and C60 Cluster Depth Profiling***, **Kateryna Artyushkova**,* Physical Electronics USA*; M. Anayee, Y. Gogotsi,* Drexel University

Two-dimensional (2D) transition metal carbides, carbonitrides, and nitrides (MXenes) have seen significant increases in the number of research areas and publications. MXenes have a unique combination of properties that have led to many applications.[1] MXenes are usually synthesized by etching "A" layers that interleave "MX" layers in the bulk MAX precursors. MAX are represented by Mn+1AXn, where M denotes early transition-metals (Ti, V, Cr, Mo, etc.), X is N or C, and A is an A-group element such as Al, Si and others. During synthesis, impurities and defects may be introduced, which significantly impact the properties of the resulting materials. It is therefore critical to detect and quantify these defects and impurities.

X-ray Photoelectron Spectroscopy (XPS) has the advantages of being easily quantifiable and providing chemical information such as surface termination and oxidation. However, there are many challenges in using XPS for analyzing MAX and Mxene. The first is a very small size of MAX, less than a few tens of microns. With the development of focused scanning micro-probe X-rays, these limitations can be overcome. The other challenge is the extreme surface sensitivity of XPS. It is challenging to separate surface adventitious carbon and oxygen from possible oxygen incorporation in the carbon site. Depth profiling using a monatomic Ar ion beam is not suitable as it can introduce damage to the structure of MAX.

In this work, we are presenting two approaches to address this challenge. The first involves the application of Hard X-ray Photoelectron Spectroscopy (HAXPES), in which a monochromated Cr X-ray source is used to probe ~3 times deeper than a soft Al X-ray. The second utilizes a cluster ion gun source, such as C60, for damage-free depth profiling through individual MAX particles using ~8µm X-ray spot for probing if oxygen is present in the MAX structure.

3:20pm **AS+2D+EM+MS+NS+SS+TF-ThA-4 Unusual Trend in Thermal Stability of Alanine Different Ni Surfaces***, J. Ontaneda,* Queen Mary University of London, UK*; R. Grau-Crespo,* University of Reading, UK*; **Georg Held**,* Diamond Light Source, UK

Chirally modified heterogeneous catalysts promise massive savings of cost and toxic waste in the production of enantiopure precursors for high-value chemicals such as pharmaceuticals, fertilizers, or fragrants [1]. A key aspect is the thermal stability of chiral modifiers, which generally are chiral organic molecules bound to a chemically active metal surface. The enantioselective hydrogenation of methylacteoacteate (MAA) is a topical reaction, which is catalysed by nickel modified with chiral carboxylic acids, such as alanine, tartaric acid, or aspartic acid [2]. The components of this catalytic system have been investigated using various surface sensitive techniques [3,4,5]. Here we present a study of the thermal stability of alanine on the three most common Ni surfaces, {111}, {100}, and {110}, using synchrotron-based temperature-programmed photoelectron spectroscopy and X-ray absorption spectroscopy. In contrast to common experience with smaller molecules, alanine is more stable on the more open {110} and {100} surfaces compared to {111}. Comparison with a detailed DFT study identifies structural and electronic effects that play a role in this unusual behaviour.

References:

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[4] P. Tsaousis, et al., J. Phys. Chem. C 122 (11) (2018) 6186 – 6194.
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[6] W. Quevedo, et al., Langmuir 36 (2020) 9399 – 9411.

3:40pm **AS+2D+EM+MS+NS+SS+TF-ThA-5 Correlative Theoretical and Experimental Study of the PC | X Interfacial Bond Formation (X = TiN, AlN, TiAlN) During DC Magnetron Sputtering***, **Lena Patterer**, P. Ondračka, D. Bogdanovski, S. Karimi Aghda, J. Schneider,* Materials Chemistry, RWTH Aachen University, Germany

Due to their outstanding oxidation and wear resistance, cubic (Ti,Al)N is widely used as protective coatings on forming and cutting tools. These characteristics make (Ti,Al)N also an attractive candidate for the protection of polymer components. The composition-induced changes in the interfacial bond formation of DC magnetron sputtered TiN, AlN, and $Ti_{0.25}Al_{0.25}N_{0.5}$ onto polycarbonate (PC) substrates are systematically investigated by correlating theory and experiment. In order to simulate the sputtering condition by *ab initio* molecular dynamics, a periodic structural model of bulk PC consisting of 394 atoms was bombarded by several Ti, Al, and N atoms with a kinetic energy of 1 eV. While both Ti and N atoms show high reactivity towards all functional groups of the polymer during the surface bombardment, Al atoms selectively react only with the carbonate group of PC or other reactive functional groups that have formed during previous bombardment events (e.g. C-N groups). At the PC | TiN and PC | TiAlN interfaces, Ti and N contribute equally to the interfacial bond formation, whereas the PC | AlN interface is defined mostly by C–N groups with Al-rich clusters forming on top of these groups. X–ray photoelectron spectroscopy data of the PC | X interfaces (X = TiN, AlN, TiAlN) show a very good agreement with the above-discussed predictions as the formation of C-N, C-(Ti,Al), and (C–O)–(Ti,Al) bonds is experimentally verified. This shows that the here employed computational strategy enables predictions of the interfacial bond formation between polycarbonate and metal nitrides, and it is reasonable to assume that the here proposed research strategy can be readily adapted to other polymer | inorganic material interfaces.

4:00pm **AS+2D+EM+MS+NS+SS+TF-ThA-6 Using Resonant Photoemission Spectroscopy to Probe the Electronic Structure of Complex Oxides with Elemental and Orbital Specificity***, **Jessica McChesney**, D. Fong, H. Hong,* Argonne National Laboratory, USA

Understanding the role of defects and interfaces is necessary in order to realize many of the promising novel properties of complex oxide heterostructure devices. To this aim, we employ resonant angle-resolved photoemission spectroscopy to probe the electronic structure with elemental and orbital specificity of complex oxide heterostructure $LaTiO_3/SrTiO_3$ (LTO/STO).Combining these spectroscopy measurements with in-situ growth characterization we are able to determine the minimum thickness required to achieve high quality heterostructures with abrupt interfaces and to correlate the formation with the 2DEG with the interface termination LTO/STO vs STO/LTO.In addition, we explore the role of oxygen vacancies in formation of the 2DEG on the bare substrate and reveal that contrary to expectations, the 2DEG is Ti^{4+} in character while the oxygen defects are Ti^{3+} in character.

Electronic Materials and Photonics Division
Room 304 - Session EM+AS+EL+NS+SS-ThA

Interfaces and Defect Engineering in Electronic & Photonic Materials & Devices

Moderator: Erin Cleveland, U.S. Naval Research Laboratory

2:20pm **EM+AS+EL+NS+SS-ThA-1 Design and Control of Defect-Mediated Properties in Electronic Ceramics***, **Elizabeth Dickey**,* Carnegie Mellon University **INVITED**

Crystalline lattice defects, e.g. vacancies, interstitials or substitutional ions, play an important role in the conductivity and dielectric properties of electronic ceramics. The material “defect chemistry” can be tuned to optimize the electronic and ionic conductivities for particular applications via doping, oxygen-activity and temperature control during processing. Beyond controlling the majority defect (carrier) concentrations, it is also important to control the minority defect concentrations as these can be especially relevant to the time-dependent electrical behavior. For example, applied electric fields in device applications provide a strong driving force for the electromigration of charged lattice defects. Furthermore, external conditions such as humidity, which can lead to proton incorporation, can also strongly influence time-dependent material properties. This talk will review our current understanding and implications of point defect equilibria, partial equilibria and dynamics in several prototypical electronic ceramics. Recent efforts to effectively co-dope dielectric materials to improve simultaneously limit both the electronic and ionic conductivity will be discussed.

3:00pm **EM+AS+EL+NS+SS-ThA-3 In-Situ Investigation of the Interface Formation between Si-Terminated Diamond and a NbxOy Electron Acceptor Layer for Electronic Applications***, **Gabrielle Abad**, P. Hopkins, S. McDonnell,* University of Virginia

Ultra-wide band gap semiconductors present one avenue for the next generation of semiconductor devices. Diamond, specifically, has shown promise in high power, frequency, and temperature electronics; however, issues with impurity doping has limited the development of diamond-based devices. Instead, surface charge transfer doping (SCTD), which avoids introduction of foreign atoms into the diamond lattice, has been used for inducing a two-dimensional hole gas at the diamond surface thus increasing its conductivity. The established method to achieve SCTD is to hydrogen-terminate the diamond surface prior to the addition of an electron acceptor layer; however, the degree of SCTD induced by H-termination is largely dependent on atmospheric exposure. Alternatively, silicon-termination of the diamond surface has been shown to produce the ordered surface with the negative electron affinity necessary for the SCTD mechanism. In this work, we investigate the combination of Si-terminated diamond with a Nb_xO_y electron acceptor layer, wherein we focus on understanding interface formation and chemistries, as well as elucidating if the band alignment mechanism is responsible for SCTD for this material system. Ultra-high vacuum (UHV) electron beam (e-beam) deposition of Si onto diamond substrates was carried out, followed by UHV annealing to produce the Si-terminated (100) diamond surface. X-ray photoemission spectroscopy (XPS) of core-level and valence band spectra was used to analyze chemical composition. To form the electron acceptor layer, Nb films were e-beam deposited onto the Si-terminated diamond surface by depositing Nb under varying oxygen partial pressures. XPS was used to observe how interfacial chemistry, electronic structure, and band alignment evolve with different Nb_xO_y compositions. The air stability of the electron acceptor layers was also investigated after atmospheric exposure via XPS. Analysis of the valence band spectra shows that band alignment would not result in SCTD for the Nb_xO_y/Si/diamond material system.

3:20pm **EM+AS+EL+NS+SS-ThA-4 Effects of Atmospheric UV-O_3 Exposure of WSe_2 on the Properties of the HfO_2/WSe_2 Interface***, **Maria Gabriela Sales**,* University of Virginia*; A. Mazzoni,* University of Maryland College Park*; W. Sarney,* Army Research Laboratory*; J. Pearson,* University of Maryland College Park*; S. Najmaei,* Army Research Laboratory*; S. McDonnell,* University of Virginia

Transition metal dichalcogenides (TMDCs) are a class of two-dimensional (2D) layered materials, in which each layer is held in-plane by strong chemical bonds, but held in the out-of-plane direction by weak van der Waals forces. For integration in an electronic device, TMDCs are typically capped in the gate region with a high-quality dielectric layer, where ultrathin (sub-5 nm) dielectric thicknesses are desired in order to achieve sufficient gate to channel electrostatic coupling. The unreactive basal plane of TMDCs makes atomic layer deposition (ALD) of dielectric films directly on top of these 2D materials challenging. In this work, we investigate the effects of atmospheric ultraviolet-ozone (UV-O_3) exposures of WSe_2 and use the UV-O_3 functionalized WSe_2 surfaces as substrates for ALD of HfO_2. We report two UV-O_3 functionalization regimes observed on WSe_2: lower exposure times, which do not result in oxidation of the WSe_2 surface, and higher exposure times, which result in a tungsten oxyselenide top layer. The properties of this oxidized layer, such as its thickness, structure, air stability, and thermal stability, are also investigated. Additionally, we note that both functionalization regimes result in variably doped WSe_2. We report on the interface chemistry observed after subsequent ALD of HfO_2, as measured with X-ray photoelectron spectroscopy (XPS). We note that variable, depth-sensitive doping states are found in the WSe_2 functionalized with higher exposure times. We also study the resultant morphologies of our deposited HfO_2 films with atomic force microscopy (AFM), and we find that both of our UV-O_3 functionalization regimes result in uniform and smooth HfO_2 films directly deposited by ALD. With the different functionalization regimes (with different interface chemistries) all providing uniform dielectric film deposition, our atmospheric UV-O_3 exposure technique on WSe_2 presents unique tunability and flexibility in the design of interfaces in devices.

3:40pm **EM+AS+EL+NS+SS-ThA-5 Near Zero Field Magnetoresistance and Electrically Detected Magnetic Resonance Studies of Instabilities in Semiconductor/ Insulator Systems***, **Patrick Lenahan**,* Pennsylvania State University **INVITED**

We have utilized both electrically detected magnetic resonance(EDMR) and near zero field magnetoresistance (NZFMR) spectroscopy to investigate the physics involved in instabilities such as stress induced leakage currents and time dependent dielectric breakdown in Si/SiO_2 and SiC/ SiO_2 systems. Both techniques are extremely sensitive and extend the sensitivity of conventional electron spin based techniques down to near nanoscale device structures. We find that the very simple spin-based NZFMR technique has significant analytical power in these investigations. The NZFMR studies can complement the more established EDMR measurements with simple and relatively inexpensive apparatus.

Fundamental Discoveries in Heterogeneous Catalysis Focus Topic
Room 321 - Session HC+AS+NS+SS-ThA

Special Session and Reception for the HC Community and to Celebrate Robert Madix

Moderators: Liney Arnadottir, Oregon State University, **Dan Killelea**, Loyola University Chicago, **Jason Weaver**, University of Florida

2:20pm **HC+AS+NS+SS-ThA-1 Gaede-Langmuir Award Talk: Not a Divide - A Continuum: Surface Science to Heterogeneous Catalysis***, **Robert J. Madix**[1],* Harvard University **INVITED**

The science of surface reactivity demands control of surface structure and surface composition. Surface science methods thus enable the investigation of reactions, including oxidations, hydrogenation, and coupling, on well-characterized single-crystal surfaces by providing molecular level insight into the bond breaking and formation on surfaces that are the basis for heterogeneously catalysis. The ultimate goal of such research is to provide benchmarks for theory, forming a firm basis for *a priori* catalyst design. In the nearer term it provides a kernel of information which can be combined with theory to accurately predict rates and selectivities for extended series of analogous reactions outside the data set. In this talk, these concepts will be discussed, linking fundamental surface science studies on Au single crystals with the performance of dilute Au-based dilute metal alloy catalysts operating at elevated temperature and 1 atm pressure. The use of key surface-science methods, including XPS, vibrational spectroscopy and temperature programmed reaction spectroscopy, will illustrate the methodology for understanding catalytic reactions. This work demonstrates the ability to successfully predict surface reactivity across vast regimes of pressure, temperature and materials complexity.

Advanced Ion Microscopy and Ion Beam Nano-engineering Focus Topic
Room 301 - Session HI-ThA

Novel Beam Induced Material Engineering and Nano Patterning

Moderators: Frances Allen, UC Berkeley, **Annalena Wolff**, Caltech

2:20pm **HI-ThA-1 Additive Nano-Manufacturing of Advanced Superconductors, and Devices Using Focused Ion Beam Technology***, **Rosa Córdoba**,* Institute of Molecular Science (ICMol), University of Valencia, Spain **INVITED**

Superconducting materials are dissipationless carriers of electric current and provide macroscopic and robust quantum coherence. These properties render them highly valuable as parts for electrical generators, magnetic sensors, and powerful magnets. To achieve the required performance employed in those applications, bulk superconductors often need nanoengineering. Moreover, when these materials are reduced to the nanoscale becoming **nanosuperconductors**, exciting new physical phenomena emerge. This has encouraged the study of their performance as 1D quantum oscillators and Josephson junction arrays as essential elements to be implemented in circuits.

Ground-breaking proposals have taken advantage of the third dimension (3D) for the development of advanced electronic components, opening fascinating novel routes in the fields of material science, physics and nanotechnology. Thus, **3D nanosuperconductors** could be implemented in future highly-efficient electronic elements. However, their fabrication and characterization remain a challenge.

In this contribution, we introduce a direct-write additive nano-manufacturing method based on focused ion beam technologies to fabricate advanced nano-superconductors at-will. This technique called focused ion beam induced deposition (FIBID) is based on CVD process assisted by an ion beam focused to a few nanometers.

We have prepared 3D superconducting hollow nanocylinders with controllable inner and outer diameters (down to 32 nm), and nanohelices with at-will geometries, by decomposing a precursor with a He^+ FIB [1,2]. These nanostrucutres become superconducting at 7 K and show large critical magnetic field and critical current density.Remarkably, these nanohelices display superconductivity up to 15 T depending on the direction of the field with respect to the nanohelix axis. This suggest that their helical 3D geometry and their orientation in a magnetic field play a significant role in the superconducting phase transition. Moreover, fingerprints of vortex and phase-slip patterns are also experimentally identified and supported by numerical simulations based on the time-dependent Ginzburg-Landau equation[3].

Additionally, we present an experimental work on the modulation of electric field-induced superconductivity in 45 nm-wide nanowires fabricated using Ga^+ FIB[4]. A theoretical model based on the GL theory explains this modulation by the squeezing of the superconducting state by the electric field.

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3:00pm **HI-ThA-3 On Demand Spatially Controlled Fabrication of Single Photon Emitters in Si**, ***Gregor Hlawacek**, N. Klingner, M. Hollenbach, U. Kentsch, G. Astakhov,* Helmholtz-Zentrum Dresden - Rossendorf, Germany

Single photon emitters (SPE) are fundamental building blocks for future quantum technology applications. However, many approach lack the required spatial placement accuracy and Si technology compatibility required for many of the envisioned applications. Here, we present a method to fabricate at will placed single or few SPEs emitting in the telecom O-band in Silicon [1] . The successful integration of these telecom quantum emitters into photonic structures such as micro-resonators, nanopillars and photonic crystals with sub-micrometer precision paves the way toward a monolithic, all-silicon-based semiconductor-superconductor quantum circuit for which this work lays the foundations. To achieve our goal we employ home built AuSi liquid metal alloy ion sources (LMAIS) and an Orsay Physics CANION M31Z+ focused ion beam (FIB). Silicon-on-insulator substrates from different fabrication methods have been irradiated with a spot pattern. 6 to 500 Si^{2+} ions have been implanted per spot using an energy of 40 keV. For the analysis and confirmation of the fabrication of true SPEs a home build photo luminescence setup has been used. G-centers formed by the combination of two carbon atoms and a silicon atom are confirmed by measurements of zero phonon lines (ZPL) at the expected wave length of 1278 nm for the case of carbon rich SOI wafers. In the case of ultra clean SOI wafers and high ion fluxes emission from tri-interstitial Si complexes is observed. The SPE nature of these so called W-centers has also been confirmed by ZPL measurements at 1218 nm. The achieved lateral SPE placement accuracy is below 100 nm in both cases and the success rate of SPE formation is more than 50%. After a discussion of the formation statistic we also present an approach how our FIB based approach can be upscaled to wafer-scale nanofabrication of telecom SPEs compatible with complementary metal oxide semiconductor (CMOS) technology for very large scale integration (VLSI).

[1] M. Hollenbach, N. Klingner, N. S. Jagtap, L. Bischoff, C. Fowley, U. Kentsch, G. Hlawacek, A. Erbe, N. V. Abrosimov, M. Helm, Y. Berencén, and G. V. Astakhov, “Wafer-scale nanofabrication of telecom single-photon emitters in silicon,” (2022), arXiv:2204.13173 [quant-ph].

3:20pm **HI-ThA-4 Towards FIB Patterning of Reconfigurable Plasmonic Arrays**, ***Ivan Kravchenko**, N. Lavrik,* Center for Nanophase Materials Sciences, Oak Ridge National Laboratory

Arrays of deterministic plasmonic nanoparticles have numerous applications in areas spanning from analytical chemistry, to catalysis, to biomedicine. E-beam lithographic patterning of metal films on inorganic substrates is a well-established technological strategy that enables implementation of 2D arrays of plasmonic particles of various shapes and arrangements with arbitrary complexity [1]. However, existing approaches to creating such arrays are limited to solid substrates that are insoluble in organic solvents since development of e-beam resists relies on the use of ketones or similar solvents that tend to attack or dissolve polymers. Here we explore a novel system in which advanced FIB milling is used to pattern arrays of plasmonic nanoparticles on a polymer film that can be liquified by increasing its temperature above its glass transition point and, therefore, provide a nanofluidic interface and, in turn, a pathway to changing the nanoparticle arrangement by external stimuli. Our initial proof of principle experiments focused on arrays of Au nanoparticles with broken symmetry (Figure 1, Supplemental Document) that can attain mobility due to photothermal or thermophoretic excitation [2].

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[1] **Gaede Langmuir Award Winner**

A Raith Velion focused ion beam/scanning electron microscope (FIB/SEM) was used to mill 25 nm thick Au film sputtered on ZEP520A electron beam resist that coated a silicon substrate. ZEP520A e-beam resist was selected as a copolymer compatible with spin coating and commonly available in a cleanroom setting. Its glass transition point of about 180C makes it a good candidate for experiments in which it can be liquified under photothermal or thermal excitation.

To avoid contamination of the Au film, the FIB milling was done by a doubly ionized gold (Au^{++}) ions at an energy of 35 kV. The beam current of 22 pA provided a sub 20 nm resolution. The dose of ion beam exposure was varied from 500 to 5000 mC/cm^2. The arrays of patterned nanoparticles were characterized by SEM, optical microscopy and Raman spectroscopy. Evolution of the nanoparticle shapes and arrangements were monitored during the FIB milling and subsequent thermal activation experiments.

Acknowledgement

This work was supported by Center for Nanophase Materials Sciences (CNMS), which is a US Department of Energy, Office of Science User Facility at Oak Ridge National Laboratory

References

1. R. Dallapiccola, A. Gopinath, F. Stellacci, and L. Dal Negro, "Quasi-periodic distribution of plasmon modes in two-dimensional Fibonacci arrays of metal nanoparticles," Opt. Express 16, 5544-5555 (2008).

2. Liu, M., Zentgraf, T., Liu, Y. *et al.* "Light-driven nanoscale plasmonic motors". *Nature Nanotech* 5, 570–573 (2010).

3:40pm **HI-ThA-5 Low Energy Ion Beam Backside Circuit Edit Applications in FinFET Devices***, M. Raza, R. Livengood , T. Malik, O. Sidorov, Z. Malamud, I. Ronen,* ***Shida Tan,*** Intel Corporation*; M. Wong,* Thermofisher Scientific

Circuit Edit (CE) using Focused Ion Beams (FIB) has been widely adopted in the industry to validate known circuit and design marginality issues, test circuit design changes, and generate engineering samples [1]. An approach, commonly known as backside CE, is to access the transistor cell and lower level interconnects of interest through the bulk silicon. The highly localized FIB milling continues until Shallow Trench Isolation (STI) region or the transistor fins are exposed. This FIB exposed trench is commonly referred to as a Node Access Hole (NAH) and it is within this area that subsequent CE tasks such as, accessing, cutting, or rerouting of lower level signals take place [2]. At the most commonly used ion beam energy of 30 KeV, Ga^+ Ion beam penetration depth, can negatively affect circuit performance by altering the intrinsic device parameters. In order to preserve the functionality of the neighboring active devices, machining geometries need to be limited by the transistor cell size and ion beam material interaction volume

An obvious approach in reducing ion material interaction volume is to operate at lower ion beam energy [3].At reduced beam energy, the lateral machining geometry can increase in size due to reduction in the ion material interaction range.In a FinFET device, the transistor channel is located at the tip of the fin, 50 to 70 nm from the bulk substrate - STI interface. Sufficient reduction in the ion beam material interaction volume also allows non-invasive machining directly over-active transistors.

In this work, we present a new approach in using low energy Ga^+ Ion beams at 5 KeV energy for NAH preparation. At low ion beam energy, we demonstrated that the NAH dimension is no longer limited by the cell size.We will present simulation data on interaction volume of the ion beams relative to the depth of the channel in FinFET, showcasing the effectiveness of low energy Ga^+ beams. Finally, we will present empirical results measuring timing impact of ion beam machining on free running ring oscillator test structures and will show example edit results on latest generation process node devices.

Plasma Science and Technology Division
Room 315 - Session PS-ThA

Harnessing the Power of Plasmas for Real-World Applications: PSTD Award Lectures

Moderators: Sebastian Engelmann, IBM T. J. Watson Research Center, **Mingmei Wang**, Lam Research Corporation

2:20pm **PS-ThA-1** ***Time-Resolved Energy and Ion Energy Distributions during High-Powered Impulse Magnetron Sputtering (HIPIMS) with Cathode Voltage Reversal , David Ruzic***[1], University of Illinois*; D. Barlaz, Z. Jeckell,* University of Illinois at Urbana-Champaign*; W. Huber, I. Haehnlein,* University of Illinois at Urbana-Champaign, Starfire Industries LLC*; T. Houlihan, B. Jurczyk,* Starfire Industries LLC **INVITED**

Reversing the potential on the cathode sputtering target immediately after the negative voltage pulse does remarkable things to the plasma, and if controlled correctly can make vastly superior thin films for a variety of applications.HIPIMS works by making a plasma dense enough to ionize the material being sputtered.Those target ions mostly return to the target and do self-sputtering.This leads to a very high current which is why the process is pulsed. Its advantages are that a small number of these ions do escape and go to the substrate, resulting in a higher ionization fraction.Its disadvantage is that fewer total atoms or ions reach the substrate resulting in a lower deposition rate.

Adding a positive voltage to the target changes everything.The plasma is expelled form the target region filling the device all the way up to the substrate being coated.This wave of plasma causes additional ionizations of the sputtered material, therefore increasing the ionization fraction reaching the substrate an increasing the deposition rate.The key though is that the plasma potential is raised by the exact voltage value of the positive pulse.This means that the ion energy reaching the substrate is controllable, without having to bias the substrate.In addition, by varying the time duration of the positive pulse with respect to the negative pulse, the ratio of target ions to working gas (Ar) ions can be controlled as well.

This talk will show detailed measurements of how this all occurs as a function of time including fast camera images.Several examples highlighting the applications made possible by such a system will be shown as well.

3:00pm **PS-ThA-3 PSTD Plasma Prize Award Talk: Plasma ON then OFF, ON - OFF, ON – OFF, ON - OFF: Who Knew Being Indecisive Could Work So Well!***,* ***Lawrence Overzet***[2]*,* University of Texas at Dallas **INVITED**

The reasons for modulating the power to a plasma can seem obvious at first. Shorter on time durations can enable one to operate at much higher instantaneous powers! One could potentially reach a power regime which is not sustainable for the same system in continuous wave (CW). In fact, one of the early papers on modulating the power to an RF plasma did so because the plasma system couldn't handle the CW heat load;[1] but then the researchers discovered something quite surprising! We tend to assume that the electron density grows as the power increases during the plasma turn-on in a somewhat “quasi-equilibrated” fashion. Further, most of us have assumed (at one point or another) that the plasma is just decaying toward zero during the off times. Slow neutral chemistry is occurring and some ion-molecule reactions too of course, but nothing all that particularly interesting or worthwhile. Even though all the above seems clear to a great majority of us, it turns out that it can be downright wrong. I've spent the greater portion of my career studying the kinetics and mechanics of how plasmas turn on and then off (and back on again) because I find those kinetics to be fascinating. (I also feel a need to state that making those measurements and models can be quite challenging!) I've found that the fashion in which energy is put into the plasma's electron population varies in time during the turn-on and turn-off. The chemical reactions can change in surprising fashions because of this and few things are as simple as one might expect. Particles confined by a CW plasma can suddenly be encouraged to leave, electron densities can increase as the power to the plasma decreases, fewer electrons can cause more reactions (and light) and plasma diagnostics can be enabled which otherwise might not even be imagined.

[1]R. Boswell and D. Henry, Appl. Phys. Lett. 47 (10) 1095-7 (1985).

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[1] **2020 AVS Gaede-Langmuir Awardee**

[2] **2021 PSTD Plasma Prize Winner**

3:40pm **PS-ThA-5 PSTD Young Investigator Award Talk: Next Generation "Birkeland-Eyde": From NH_3 to NO*, Floran Peeters*[1]*,*** DIFFER, Netherlands **INVITED**

In 1905 industrial-scale production of nitric acid began in Notodden, Norway. This development came in response to a global shortage of nitrogen fertilizer, required to feed the world. Where for years nitrogen fertilizer was obtained by harvesting diminishing supplies of guano, several initiatives were undertaken to produce nitrogen fertilizer artificially. Scientists and engineers in the US and in Europe independently developed nitrogen fixation methods based on breaking the strong molecular nitrogen bond using electric arcs, forming NO as an intermediate chemical. Sustaining arc discharges continuously, a definite requirement for commercial exploitation, leads to electrode sputtering and thus a limited lifetime of the reactor. This problem was solved by Birkeland and Eyde by rotating the arcs in a magnetic field, leading to a 40 MW nitrogen fixation plant which remained operational until the 1920's.

Starting in the 1910's the use of electric arcs for the fixation of nitrogen was slowly overtaken by the more energy-efficient catalytic Haber-Bosch process, in which NH_3 is formed from atmospheric nitrogen and hydrogen from natural gas. This high temperature, high pressure process, while an engineering marvel in its own right, suffers from a major drawback when viewed through a modern lens: its heavy reliance on fossil fuels.

With the global aim of transforming the chemical industry to rely on sustainably generated electricity,interest in fixing atmospheric nitrogen using only electrical power has gained renewed interest. In this contribution, an analysis will be given of the existing nitrogen fixation production chains and the possibilities and benefits of replacing these with new, plasma-based methods. Using insights gained from over a century of scientific literature, recent experiments and models, strategies for improving plasma-based nitrogen fixation methods will also be discussed.

Quantum Information Science Focus Topic
Room 302 - Session QS+EM+MN+NS-ThA

The Quantum Metrology Revolution

Moderator: Dave Pappas, Rigetti Computing

2:20pm **QS+EM+MN+NS-ThA-1 Magnetic Textures in Quantum Materials Revealed by SQUID-on-tip Microscopy*, Ella Lachman,*** Rigetti Computing **INVITED**

Quantum materials are rapidly emerging as the basis for possible novel computation devices. However, fully understanding the interplay between magnetic and electronic excitations prevents us from realizing their full potential. In my talk, I will present the nano-SQUID-on-tip device and the scanning microscope built around it. Originally built to study superconducting vortex dynamics, this microscope has unprecedented magnetic sensitivity and spatial resolution.

I will show how expanding the microscope's range and realizing the microscopic magnetic textures in quantum materials is crucial to the understanding of transport phenomena on the macro scale. This will be demonstrated with two examples from two different types of materials. First, I will show how scanning nanoSQUID-on-tip magnetic imaging of magnetically doped topological insulators reveals the underlying fragility of the Quantum Anomalous Hall effect at elevated temperatures. Then, I will show how with a combination of transport, magnetization, and magnetic imaging of the Weyl semimetal $Co_3Sn_2S_2$, we find that the dynamics of domain walls are responsible for the anomalous transport behavior in the material.

These examples show that better understanding of the microscopic magnetism in these systems reveal new phenomena and deepen our understanding of the interplay between magnetic textures and electronic properties.

3:00pm **QS+EM+MN+NS-ThA-3 Quantum-Based Measurements for Pressure and Vacuum and the NIST on a Chip Program*, Jay Hendricks,*** *B. Goldstein,* NIST

The world of pressure and vacuum measurements and standards is currently undergoing a revolution in both measurement traceability, "the fundamental philosophy behind a measurement chain back to primary units", and measurement technology, the "how a measurement is made".This keynote presentation covers a bit of metrology history of how we got to where we are today and gives a forward-looking vision for the future.The role of NIST as a National Metrology institute is described along with an explanation of how and why our world-wide standards changed on May 20th, 2019.The NIST on a Chip program (NOAC) is introduced which seeks to utilize fundamental physics and laws of nature to develop quantum-based sensors and standards that one day may be miniatured to the chip scale.The technical core of the lecture will be a deeper dive into new research on measurement methods for pressure, the Fixed Length Optical Cavity (FLOC) and for vacuum, the Cold Atom Vacuum Standard (CAVS).What is exciting about these new measurement approaches is that they are both primary (relying on fundamental physics), are quantum-based and use photons for the measurement readout which is key for taking advantage of the fast-growing field of photonics. The FLOC will enable the elimination of mercury barometers pressure standards worldwide and the CAVS will be first primary standard for making vacuum measurements below 1.3x10-5 Pa.

3:20pm **QS+EM+MN+NS-ThA-4 Materials and Devices for Efficient Quantum Memories and Sensors*, Lee Bassett,*** University of Pennsylvania **INVITED**

Certain point defects in semiconductors exhibit quantum-mechanical features comparable to isolated atoms or molecules, in a solid-state materials platform amenable to nanofabrication, heterointegration with other materials and classical devices, and large-scale system engineering. Well-known quantum point defects such as the diamond nitrogen-vacancy center are leading candidates as robust quantum memories, versatile quantum sensors, and efficient light-matter interfaces. Meanwhile it is increasingly clear that alternative materials and defect systems offer potential advantages and new capabilities for quantum science [1]. However, millions of potential defects exist, and their identification is often tedious and challenging. This talk will introduce the opportunities and challenges of identifying point defects, including several new approaches to efficiently predict, characterize, and engineer their properties for quantum science and technology.

[1] L. C. Bassett, A. Alkauskas, A. L. Exarhos, and K.-M. C. Fu, "Quantum defects by design" Nanophotonics 8, 1867 (2019).

Funding: We acknowledge support from the NSF (DMR-1922278 and DMR-2019444).

Advanced Surface Engineering Division
Room 317 - Session SE+AS+MN+SS-ThA

Mechanical and Tribological Properties of Thin Films and Coatings

Moderators: Jyh-Wei Lee, Ming Chi University of Technology, Taiwan , **Filippo Mangolini**, The University of Texas at Austin

3:00pm **SE+AS+MN+SS-ThA-3 Differential Impact of Scale Dependent Roughness on Lubricant Infused Surfaces*, Robert Chrostowski*,** *B. Fang, J. Smith, F. Mangolini,* University of Texas at Austin

Lubricant Infused Surfaces (LIS), which consist of an engineered surface texture with an absorbed lubricant, have recently emerged as an innovative approach for achieving pressure-stable omniphobicity and for improving tribological performance in the presence of external contaminants. The design of successful LIS heavily relies on the effect of surface texture, which is quantified using a single dimensionless parameter, namely the ratio of the true surface area to the nominal surface area. Previous published studies have thus focused on the evaluation and optimization of microscale pattered morphologies with simple geometries (for which the ratio of the true surface area to the nominal surface area can be determined analytically), such as ordered arrays of pillars. Texture, however, is defined both by these larger-scale structures, and by smaller sub-micron scale asperities called roughness. Roughness can exhibit scale-dependent fractal self-similarity, and the absolute finest scales of roughness can have outsize impact on the quantitative value of the area ratio. Despite the scientific relevance of previous studies on fractal surfaces and the effect of roughness on contact mechanics, our understanding of the effect of surface roughness on the retention of a lubricant is elusive.

Here, we evaluate the lubricant infusion behavior of two different fluorinated polymer lubricants of substantially different molecular size, but similar surface chemistry, on fractal nano-rough boehmitized aluminum surfaces. Power spectral density (PSD) analysis of atomic force microscopy

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[1] **2021 PSTD Young Investigator Awardee**

(AFM) topography maps is used to estimate the area ratio for each surface at the length scale of the radius of gyration of the different lubricants. The area ratio values computed from the PSD are then related to true area value that matches predicted spin-coating curves to observed gravimetric ones. The experimental results demonstrate, for the first time, the impact of fractal roughness on the shear-retention of LIS.

The outcomes of this work, providing evidence that different molecular length fluids could experience different quantitative magnitudes of roughness on the same, significantly contribute to our understanding of the impact of scale-dependent roughness on the retention of liquids on engineered surface textures, while enhancing the scalability of LIS systems and their cost-effective implementation in several technological applications.

3:20pm **SE+AS+MN+SS-ThA-4 Imperfectly Perfect Coatings for Rolling Bearing Applications***, **Esteban Broitman**,* SKF B.V. - Research and Technology Development, Netherlands **INVITED**

Machines with rotating components usually rely on bearings to reduce friction in moving its parts around a fixed axis. The increasing demand for more precise bearings to lower power consumption and heat generation, while simultaneously support increasing applied loads and/or higher speeds, has given place to the use of surface engineering processes.

In the case of bearings, it is widely accepted the advantages of using coatings as the surface process to improve its performance. During the last three decades, advanced coatings have enjoyed a growing interest in several industrial applications because they can be engineered to provide different properties like electrical insulation, low friction, and resistance to corrosion, plastic deformation, etc.

In this talk I will compare the structural, mechanical and tribological properties of two coatings that are used nowadays to improve the performance of rolling bearings made of standard bearing steel: they provide lower friction, resistance to surface initiated rolling contact fatigue, and decreased wear: NoWear® (a carbon-based nanostructured coating made by plasma-assisted chemical vapor deposition PACVD) of about 3 µm-thick, and Black Oxide (an iron oxide film made by a chemical conversion method) of about 1 µm-thick. Being coatings produced by different techniques, both have a common feature: they are *"imperfectly perfect coatings."* Scanning electron microscopy, X-ray photoelectron spectroscopy, and nanoindentation measurements show that, from the microstructural point of view, these coatings are full of *"imperfect"* features, like cracks, voids, porous, columns, and other naughty irregularities. The different mechanisms contributing to the positive tribological behavior of each coating under lubricated conditions will be discussed. I will demonstrate that these coatings, taking advantage of their own different *"imperfect"* features, behave *"perfectly"* from the tribological point of view, and therefore can successfully be used to extend maintenance and life expectancy of specialized rolling bearings.

4:00pm **SE+AS+MN+SS-ThA-6 Tribological Behavior of WC/WCN/CNx Thin Films Deposited by HIPIMS***, **Luis Flores-Cova**, O. Jimenez, M. Flores,* Universidad de Guadalajara, Mexico

Coatings and thin films are used to protect against wear in many applications. If that coating also shows a low coefficient of friction, it brings better benefits, therefore, the research on coatings with these properties is of great interest. In this respect, carbon containing, or carbon-based coatings are the most popular. 52100 alloy used in wear environments has its own disadvantages. Consequently, many coating systems have been deposited on this alloy to improve its wear resistance. In this study, a multilayer coating with carbon content (WC/WCN/CNx) was deposited by High Power Impulse Magnetron Sputtering (HiPIMS) on AISI 52100 alloy. No external heating was applied during the deposition, energetic tungsten ions increase adatoms mobility that enhance adhesion. The thickness and the growth morphology of the films were studied from FE-SEM cross-sectional images. The chemical composition was analyzed by XPS. The structure of the coatings was analyzed by XRD technique. The mechanical properties (hardness and Elastic Modulus) were studied through nanoindentation techniques. The adhesion of coatings to the substrate was measured by means of scratch tests. Wear tests were performed using a tribometer with a pin on disc configuration, using a 10 mm diameter 52100 ball. The wear tracks were analyzed by SEM and the wear volume was obtained by optical profilometry. The coating showed a coefficient of friction lower than 0.3 and the wear rate was reduced 100 times relative to the substrate.

Surface Science Division
Room 319 - Session SS+AS+SE-ThA
ALD and CVD Surface Chemistry

Moderators: Melissa Hines, Cornell University, **Dario Stacchiola**, Brookhaven National Laboratory

2:20pm **SS+AS+SE-ThA-1 ALD Surface Chemistry on Lithium-Ion Battery Cathodes***, **Jeffrey Elam**,* Argonne National Laboratory **INVITED**

Next-generation energy storage devices demand superb control over interfaces. Atomic layer deposition (ALD) is a powerful strategy for controlling interfacial properties. ALD coatings can suppress undesirable electrochemical reactions between lithium-ion battery (LIB) cathode surfaces and the organic liquid electrolyte and improve LIB cycling stability. While numerous reports have evaluated the electrochemical performance of ALD treated cathode materials, the chemical changes induced on the surface of the cathode materials by the ALD coatings and the individual ALD precursors are not fully studied. This presentation highlights our recent work investigating the surface chemistry of ALD on LIB cathode surfaces. We find that the nucleation and growth of Al_2O_3 ALD on$LiMn_2O_4$ (LMO) is much different compared to conventional surfaces such as hydroxylated SiO_2. For instance, LMO does not have surface hydroxyls under typical ALD conditions. During initial Al_2O_3 ALD cycles, trimethyl aluminum reacts with Mn-O bonds and reduces surface Mn ions generating C_2H_6. Al_2O_3 ALD on LMO is highly precursor-dependent and the degree of surface Mn reduction is strongly influenced by the Lewis acidity of the precursor ligands. In addition, the Al_2O_3 ALD growth per cycle (GPC) on LMO varies by 30x among 5 Al_2O_3 ALD precursors that exhibit essentially the same GPC on SiO_2. We next examined the surface chemistry for Al_2O_3 and AlF_3 ALD on 12 different cathode surfaces ranging from simple transition metal oxides (e.g., NiO and MnO) to complex multi-element cathode materials (e.g., $LiNi_xMn_{1-x-y}Co_yO_2$, NMC). We found that the Ni, Mn, and Co transition metals in the cathode undergo selective oxidation/reduction depending upon the nature of the precursor, the coating, and the cathode material. Furthermore, our measurements revealed the conversion of surface carbonate species to the corresponding metal fluorides upon HF exposure. This conversion reaction is self-limiting but extends hundreds of nanometers below the surface in the case of Li_2CO_3. ALD and chemical vapor treatment provide new avenues to systematically control the interface of the cathode materials in LIBs that are not possible by conventional coating methods.

3:00pm **SS+AS+SE-ThA-3 Role of Temperature, Pressure and Surface Oxygen Migration in the Initial Atomic Layer Deposition of HfO_2 on Anatase TiO_2(101)***, G. D'Acunto, R. Jones,* Lund University, Sweden*; L. Pérez Ramírez,* Synchrotron Soleil, France*; P. Shayesteh, E. Kokkonen, F. Rehman,* Lund University, Sweden*; F. Lim, F. Bournel, J. Gallet,* Sorbonne Université, France*; R. Timm, **Joachim Schnadt**,* Lund University, Sweden

Atomic layer deposition (ALD) has become one of the prime methods for deposition of ultrathin films with atomic-scale precision [1,2]. Yet, for many ALD processes the underlying surface chemistry or aspects of it remain unclarified [3,4]. Experimental methods that allow the real-time monitoring of the ALD surface chemistry, i.e. time-resolved methods that can be applied during an ongoing ALD process, can provide much deepened insight into the ALD surface chemistry. One such method is time-resolved ambient pressure x-ray photoelectron spectroscopy (APXPS), which is an excellent match to ALD since it easily can be used in standard ALD pressure conditions of up to around 1 mbar. Here, we have applied APXPS to the study of the surface chemistry of the initial full cycle of HfO_2 ALD on TiO_2(101) from tetrakis(dimethylamido) hafnium (TDAMHf) and water precursors at both high (500 K) and low (300 K) surface temperature as well as high (~10^{-1} mbar) and low (~10^{-6} mbar) pressure.

Generally, we find that the initial ALD process on TiO_2(101) is characterised by an absence of surface hydroxyls, which implies that the reaction cannot proceed via the ligand-exchange mechanism standardly proposed for oxide ALD from amido complexes and water. Instead, dissociative adsorption and subsequent hydrogen insertion reactions take place during the first metal half-cycle, which lead to the formation of a number of different surface species, including a dimethyl ammonium ion and an imine. Their formation requires either a bimolecular reaction pathway or an active role of the TiO_2(101) surface as an oxygen supplier. Both pathways are viable and may compete with each other. Oxygen transport is evident from the formation of HfO_2 during the very first half-cycle and a concomitant reduction of the TiO_2 support already. The water half-cycle then allows hydroxyl formation, but only at sufficiently higher water pressure. In this case, a transition towards a ligand exchange reaction mechanism is possible, which, however, is hindered if the water pressure is too low.

Our study highlights how chemical models for transition metal oxide ALD from amido complexes and water need to be extended, by consideration of hydroxyl-free surfaces, oxygen transport and bimolecular reactions paths, and how time-resolved *in situ* studies can help understand how deposition parameters affect the growth of HfO_2.

[1] Miikkulainen, V.; Leskelä, M.; Ritala, M.; Puurunen, R. L. *J. Appl. Phys.* 2013, **113**, 021301

[2] Johnson, R. W.; Hultqvist, A.; Bent, S. F. *Materials Today* 2014, **17**, 236

[3] Zaera, F. *Coord. Chem. Rev.* 2013, **257**, 3177

[4] Richey, N. E.; De Paula, C.; Bent, S. F. *J. Chem. Phys.* 2020, **152**, 1

3:20pm **SS+AS+SE-ThA-4 ALD of Well-Defined Mixed-Oxide and Metal-Oxide Catalytic Interfaces*, Francisco Zaera,*** University of California - Riverside

As the chemistry of solids is in most instances determined by the nature of their surfaces, control over the nature of surface sites during preparation is critical to the design of materials for specific applications. This is a difficult task, especially when complex multicomponent atomic ensembles are required. In this presentation we illustrate how atomic layer deposition (ALD) may be used to prepare such sites. We will describe the development of prototypical surface sites comprised of mixtures of silica supports (mainly well-structured mesoporous materials such as SBA-15), titania thin films, and gold nanoparticles, as that combination has proven to offer some unique and useful surface chemistry for low-temperature catalysis. The materials resulting from the use of ALD approach have been characterized using a surface-science approach, relying on the use of adsorption-desorption isotherms and well-defined mesoporous structures together with electron microscopy and a variety of spectroscopic techniques, including IR, NMR, XPS, EPR, and Visible-UV absorption. They showed some unique redox properties, and were tested for the promotion of low-temperature oxidation and selective hydrogenation reactions. Time permitted, other mixed-oxide interfaces, in particular silica-alumina, will be introduced as well.

3:40pm **SS+AS+SE-ThA-5 Mechanistic studies on Catalytically Activated ALD of Fe_2O_3 on Pt*, Andreas Werbrouck,*** Stanford University, Belgium*; J. Schneider, S. Nathan, A. Rothman, S. Bent,* Stanford University

Atomic layer deposition (ALD) of Fe2O3 is well-studied process. Fe2O3 has numerous applications, for example in catalysis or as a ferroelectric material. While many Fe2O3 ALD processes have been reported, almost all of those use an iron precursor in combination with strong oxidizers such as H2O2, O3, or O2 plasma. Recently, ALD of Fe2O3 on Pt substrates has been demonstrated using just O2 gas as the co-reactant, with tert-butyl ferrocene (TBF) as the metal precursor [1]. The process was area selective, with no growth occurring on other substrate materials (SiO2, Al2O3, Au); hence, it is hypothesized that the Pt substrate creates reactive oxygen species in situ, effectively catalyzing the reaction to grow Fe2O3. Intriguingly, the activation continues after the Pt substrate has been completely covered by Fe2O3. The continued growth is attributed to the formation of a sub-surface oxygen reservoir.

In this work, we further investigate this process, with a focus on the underlying oxygen activation and transport mechanisms. In situ ellipsometry was used to study the growth characteristics and x-ray diffraction confirmed the Fe2O3 crystal structure. X-ray photoelectron spectroscopy results show a clear correlation between the amount of deposited Fe2O3 and the Pt surface coverage. To study the kinetics and mechanistic steps of the process, quadrupole mass spectrometry (QMS) was employed. H2O (m/z 18) CO (m/z 28, which is also N2) and CO2 (m/z 44) are observed as reaction products when Pt is present, indicating a combustion-like mechanism. Furthermore, as expected, the kinetics of the reservoir change as the film grows thicker; this behavior is confirmed by the QMS measurements.

Finally, a simple 1D diffusion model was developed to describe the sub-surface oxygen reservoir process (fig. 1). Given the partial pressure of O2, the model captures adsorption, transport and desorption of the oxygen in the layer before (O2) and after (O*) activation. The Pt surface coverage is parametrized too. The model yields observable outputs such as the amount of desorbing species and reaction products, but also parameters which are harder to access experimentally, such as the activation energies and kinetic constants and concentrations of the different species in the layer. Comparison of the model results with experimental data should help provide deeper insight into the mechanism of catalytically activated ALD.

[1] Singh, Joseph A., et al. "Area-selective atomic layer deposition of metal oxides on noble metals through catalytic oxygen activation." Chemistry of Materials 30.3 (2018): 663-670.

Thin Films Division
Room 316 - Session TF+AS-ThA
In-Situ Characterization of Thin Films and Interfaces

Moderators: James Fitz-Gerald, University of Virginia, **Robert Grubbs**, IMEC Belgium

2:20pm **TF+AS-ThA-1 *In situ* IRRAS and XPS for the Characterization of Gas Interactions with MOF Nanofilms*, Tianhao Hu,*** Stony Brook University/Brookhaven National Laboratory*; C. Eads,* Max IV Laboratory, Sweden*; D. Stacchiola, A. Head,* Brookhaven National Laboratory

The need for novel solid catalysts for use in industry has demanded the development and the application of new techniques of *in situ* spectroscopy which enables the study of catalysts in conditions close to industry. Infrared spectroscopy and X-ray photoelectron spectroscopy (XPS) are complementary techniques that provide chemical and electronic structure information and have been widely used under *in situ* conditions. However, applying these techniques to insulating powders, such as metal-organic frameworks (MOFs), in controlled environments can be challenging. Here we grow films of archetypical MOFs, UiO-66 and UiO-66(NH_2), via a vapor-assisted conversion method and incorporate Pt catalytic sites (Pt@UiO-66(NH_2)) through solution impregnation. Using ambient pressure XPS, the electronic structure of the MOF and the oxidation state changes of the Pt are followed under various gas dosing conditions. Using infrared reflection absorption spectroscopy (IRRAS) and the adsorption of probe molecules N_2, CO, CO_2, and ethylene, under-coordinated metal sites and the acid strength of hydroxyl groups are characterized. IRRAS was also used to follow the oxidation of CO catalyzed by Pt@UiO-66(NH_2). Signature IR bands for gas phase CO_2 product and CO interacting with Pt^0 sites at 2024 cm^{-1} and 2098 cm^{-1} are found. This study highlights the information to be gained by applying traditional surface science techniques to nanoscale films for chemical, electronic, and reactivity characterization.

2:40pm **TF+AS-ThA-2 AVS Nellie Yeoh Whetten Awardee Talk: Characterizing Early-Stage Morphology and Defect Dynamics in Block Copolymer Thin Films with Environmentally Controlled High-Speed Atomic Force Microscopy*, Julia Murphy*[1]*,*** University of Chicago*; J. Raybin,* University of California at Berkeley*; S. Sibener,* University of Chicago

The spontaneous self-assembly of block copolymers into a variety of nanoscale morphologies makes these systems ideal candidates for next-generation lithography applications. However, industrial application requires long-range control over the domain order and orientation. Extensive work has been done to achieve linearity in nanopatterns on wafer size scales, but there is also a need to control the formation of point defects to generate, for example, T-junctions, jogs, and bends for semiconductor templating applications. As such, a fundamental understanding of block copolymer nanopattern formation and how structural defects contribute to instability in the films is crucial to achieve the perfection required to utilize these thin films as lithographic templates for nanotechnologies. Here, I present recent work on poly(styrene-*block*-methyl methacrylate) (PS-*b*-PMMA) thin films with environmentally controlled high-speed atomic force microscopy (AFM). By imaging films with minor variations in thickness above the glass transition temperature, we capture the early formation of hole, island, and continuous relief structures during thermal annealing. Additionally, we see how the striped nanoscale pattern develops in tandem with the changing mesoscale features. Confining the PS-*b*-PMMA in lithographic templates that are tapered in width, or wedge-shaped, generates dislocations at precise intervals locations in otherwise linearly aligned polymer domains. Examining polymer confined in these films reveals the pathways by which dislocations evolve and annihilate during thermal annealing, and how point defects in nanopatterns influence interfacial fluctuations in the surrounding polymer domains. Together, these studies contribute to the fundamental understanding of the dynamics and ordering of block copolymer thin films and reveal how topography - both native and imposed by lithography – impacts the nanoscale structure.

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[1] **AVS Nellie Yeoh Whetten Awardee**

3:00pm **TF+AS-ThA-3 *In Situ* X-Ray Scattering Studies of the Influence of Plasma Properties on Epitaxial InN Growth by PEALD*, Jeffrey Woodward,* ***S. Rosenberg, D. Boris,* U.S. Naval Research Laboratory*; M. Johnson,* Syntek Technologies*; S. Walton, S. Johnson,* U.S. Naval Research Laboratory*; Z. Robinson,* SUNY Brockport*; N. Nepal,* U.S. Naval Research Laboratory*; K. Ludwig,* Boston University*; J. Hite, C. Eddy,* U.S. Naval Research Laboratory

Plasma-enhanced atomic layer deposition (PEALD) enables the epitaxial growth of ultrathin indium nitride (InN) films at significantly reduced temperatures and with atomic-level control of layer thickness. These advantages are challenged by the inherent complexity of the growth process due to the reliance on plasma surface interactions [1], which necessitates a detailed understanding of the relationship between the plasma and the growth kinetics. To this end, synchrotron hard x-ray scattering techniques are well-suited to the *in situ* study of PEALD processes, as they are capable of operating in harsh environments during chemical reactions and can provide real-time information about the structural properties of the film. One such technique, grazing incidence small-angle x-ray scattering (GISAXS), probes nanoscale fluctuations in electron density averaged across the sample, which can provide an in-depth description of surface topography [2]. Initial studies of epitaxial InN growth under fixed plasma conditions demonstrated the utility of GISAXS for understanding the kinetics of PEALD processes, and showed that the growth proceeded in a Stranski-Krastanov mode where the critical thickness for island formation and the coarsening behavior were strongly influenced by temperature [3].

In this work, we utilize *in situ* GISAXS to investigate the early-stage PEALD growth kinetics of epitaxial InN within three different plasma regimes. The GISAXS data are supported by diagnostic studies of the plasma species generation in the inductively coupled plasma source as a function of the relative concentrations of the nitrogen/argon gas mixture used in the growth process. The growth mode is found to be correlated to the production of nitrogen species in the plasma, with high concentrations of atomic N species promoting Volmer-Weber growth and low concentrations promoting Stranski-Krastanov growth. Under conditions of high atomic N production, both the island radius and critical thickness for island formation are found to increase with ion flux. Furthermore, the InN island distance and areal density are found to change only during plasma exposure, and to continue changing with exposure even after the methylindium adlayer is believed to have fully reacted with the plasma. Our results demonstrate the potential to control the growth kinetics during PEALD of epitaxial films by intentionally accessing specific regimes of plasma species generation.

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3:20pm **TF+AS-ThA-4 Optical Monitoring of $MoCl_5$ and H_2S Delivery During Atomic Layer Deposition of MoS_2*, Berc Kalanyan,*** National Institute of Standards and Technology*; E. Jahrman,* National Institute of Standard and Technology*; J. Maslar,* National Institute of Standards and Technology

Low-temperature (<400 °C) deposition of transition metal dichalcogenide (TMD) films has been proposed as a potential route for fabricating diffusion barrier structures in field effect transistors and other electronic devices. Atomic layer deposition (ALD) is well-suited to this application due to its low thermal budget and high conformality, enabling its integration into back-end of line processing. Several publications have described the deposition of layered MoS_2 films by ALD, most commonly using $MoCl_5$ and H_2S as precursors[1–4]. Inorganic precursors may be desirable for their high thermal stability and the lack of organic ligands, which often are a source of impurities in deposited films. However, $MoCl_5$ is a low-volatility solid under typical delivery conditions and can readily form oxychlorides upon exposure to moisture. Delivery challenges associated with $MoCl_5$ are reflected in the large variety of delivery methods and conditions reported in the literature, for instance a vessel temperature range of 70 °C to 210 °C. Deposition studies using $MoCl_5$ and H_2S also show inconsistent results with respect to MoS_2 morphology, grain size, and composition, with no deposition reported under some conditions[5]. This lack of reproducibility could stem from variations in $MoCl_5$ flux observed under different delivery configurations. To address this possibility, we monitored the flow of $MoCl_5$ and H_2S as a function of delivery conditions using direct absorbance measurements. We measured vapor phase spectra of neat $MoCl_5$ and its common oxychlorides using an ultraviolet-visible (UV-vis) spectrometer under static conditions. To evaluate precursor delivery under flow, we implemented in-line gas analyzers each consisting of a broadband source, a filter for wavelength selection, and an avalanche photodiode. We evaluated the delivery rates of $MoCl_5$ and H_2S injected from vapor draw and direct draw vessels, respectively. In addition to vapor phase measurements, we used real-time spectroscopic ellipsometry to characterize precursor adsorption under varying delivery conditions. Using results from these measurements, we will discuss the reproducibility of $MoCl_5$ and H_2S delivery rates and potential implications for MoS_2 deposition.

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3:40pm **TF+AS-ThA-5 Temperature-Time-Thickness (TTT) Topography Maps: A Parameter Space Visualization Approach for ALD Processes*, S. Novia Berriel,*** *C. Feit, U. Kumar,* University of Central Florida*; A. Arunachalam,* University of Texas at Dallas*; S. Seal,* University of Central Florida*; K. Basu,* University of Texas at Dallas*; P. Banerjee,* University of Central Florida

In atomic layer deposition (ALD), an optimized process is characterized by its stability, predictability, and self-limiting nature. Each of these characteristics is quantified individually with separate sets of experiments. For stability, temperature is varied while holding pulse time constant. Similarly, a process's self-limiting nature is determined by saturation curves, varying the pulse time (i.e., dose) of the precursors while holding temperature constant. These data are usually presented in such as way as to imply no interdependency between them. This is a limited view of process optimization that will only yield partial understanding of deposition characteristics. We propose the information held in the interdependencies of these parameters can lead to improved process development and better control of final film properties.

We have used in situ spectroscopic ellipsometry to capture temperature-time-thickness (TTT) topography maps of ALD processes. The TTT contour plots are 3D visualization maps that demarcate dose saturation times, temperature windows, and corresponding growth rates. Based on a methodology recently published by our group[1], we demonstrate TTTs of several thermal ALD processes including CeO_2, Al_2O_3, ZnO, TiO_2, as well as plasma enhanced ALD (PEALD) of TiO_2. These topographies collectively show stability, adsorption, and reaction (i.e., thermodynamic) characteristics of the precursor reactant molecules. TTT curves are also obtained as single-substrate experiments, thus reducing process development times and resource consumption. We propose a comprehensive database of TTT diagrams can be used for improved process development and can eventually provide guidance towards the development of precursors finely tuned to the requirements of ALD processes.

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4:00pm **TF+AS-ThA-6 Surface Functionalization of Cu with Inhibitors to Enable Area-Selective Atomic Layer Deposition*, Andrew Kaye,*** *S. Agarwal,* Colorado School of Mines

Area-selective atomic layer deposition (AS-ALD) is a bottom-up fabrication technique that can address challenges related to conventional lithography in the fabrication of integrated circuits. Cu is the predominant interconnect metal while SiO_2 is used as the dielectric. In this work, we explore the growth of a dielectric on SiO_2, with Cu as the nongrowth surface. Using *in situ* reflection-absorption infrared spectroscopy (RAIRS) we previously showed that thiols are effective inhibitors for Cu, and readily adsorb onto the surface by reducing the native CuO_x layer. However, thiols have a low vapor pressure and thermal stability on Cu. With these inhibitors, the Cu surface can be re-dosed between ALD cycles, which is essential in plasma-assisted ALD processes. Moreover, the inhibitor readily desorbs from the non-growth surface after AS-ALD, which eliminates surface cleaning steps that are normally required with self-assembled monolayers. Recently, several small molecule inhibitors for Cu have been reported in the AS-ALD literature including alkynes, aniline, and pyridine.

For alkynes, we show that a H_2 plasma cleaning step is required to reduce the native CuO_x layer on the Cu surface. When Cu wafers left in atmospheric conditions are exposed to an H_2 plasma, RAIRS shows that surface carbonates are removed, which indirectly confirms the presence of surface CuO_x. Specifically, we show that after we optimized the H_2 plasma cleaning duration at 200 °C, 5-decyne adsorbs on the Cu surface. The adsorption of 5-decyne is apparent from the appearance of –C=C– and –C≡C– stretching vibrations in the ~1600 and ~2200 cm^{-1} regions, respectively. In addition, we also observed the CH_x stretching and bending modes in the ~2900 and ~1400 cm^{-1} regions, respectively. Adsorption of 5-decyne on PVD and CMP Cu was observed over the temperature range of 28 to 150 °C. As the substrate temperature increased for the PVD Cu surface, the intensity of the –C=C– mode decreased while the –C≡C– mode increased, indicating that chemisorption is favored at lower temperatures while strong physisorption is favored at higher temperatures. At higher temperatures, the CH_x stretching and bending mode intensities decreased, indicating lower 5-decyne adsorption. ALD of Al_2O_3 on Cu with 5-decyne as an inhibitor was tested with dimethyl aluminum isopropoxide (DMAI) and H_2O. Even at sub saturation doses of DMAI, AS-ALD was not observed. We will also compare 5-decyne as an inhibitor with aniline and pyridine, which have been demonstrated as more promising candidates.

2D Materials Technical Group
Room Ballroom A - Session 2D-ThP

2D Materials: Poster Session

2D-ThP-1 MoS_2 on Sapphire for Aligned Growth Using Liquid Precursor, ***Anindita Chakravarty,*** University at Buffalo

Aligned growth of MoS2 has been a hot topic for research due to the high quality of two dimensional (2D) films obtained by Chemical Vapor Deposition (CVD). This research paper demonstrates aligned growth of MoS2 on sapphire using liquid precursors. Importance of parameters like oxygen plasma etching, amount of precursor used and low temperature annealing has been experimented with in this research. It has been determined that the sapphire used should be c-type , and needs to have a relatively smooth surface for growth of aligned MoS2 on it. The bond between the substrate and the flakes plays a significant role on the properties of the material grown. To test the quality of the flakes, ionic liquid has been used as a side gate. Electronic properties were measured after directly performing electron beam lithography and metal deposition onto the sapphire substrate containing the flakes.

2D-ThP-2 Growing and Analyzing Ultra-Thin Polyaniline Films, ***Anthony Annerino,*** *P. Gouma,* The Ohio State University

Presented here are investigations on the growth and analysis of ultra-thin polyaniline films. Polyaniline is a highly studied intrinsically conducting polymer that has shown promise in a wide variety of applications but still proves relatively difficult to process on account of its negligible solubility in all but the most toxic organic solvents. This work aims at highlighting an uncommon avenue of polyaniline processing with great promise for many applications. Polyaniline films described here are grown via oxidative polymerization on the surface of an aqueous solution, and growth parameters including growth time, available growth area, and starting material concentrations are evaluated for their effects on various properties of the resultant films. Properties investigated include electrical properties, thermal properties, and film thickness.

2D-ThP-3 Modification of Bilayer VSe_2 by Intercalating Transition Metals, ***Vimukthi Pathirage,*** *K. Lasek, J. Li, I. Ponomareva, M. Batzill ,* University of South Florida

Transition metal dichalcogenides (TMDs) are prototypical van der Waals materials that can be grown as ultrathin films and/or van der Waals heterostructures. While TMDs exhibit a variety of properties, they are usually non-magnetic.[1] Metal intercalation in between TMDs may be a process to introduce magnetism and thus design magnetic van der Waals materials.

Here we explore the possibility of controlling the intercalation of transition metals into ultrathin VSe_2 films in an attempt to modify their magnetic properties and to design magnetic van der Waals heterostructures. VSe_2 mono- to few-layer films are grown by van der Waals epitaxy on HOPG or MoS_2. These films are subsequently modified by post-growth deposition of transition metals, such as Cr. Our scanning tunneling microscopy (STM) studies indicate that the deposited Cr reacts with monolayer VSe_2 and forms complex ad-atom structures. In contrast, for bi- and multilayer VSe_2 the Cr-deposition maintains an atomic corrugation of the VSe_2 layer, however, the periodicity changes to a 2x1 structure with respect to VSe_2 lattice. This additional superstructure is interpreted as caused by the intercalation of Cr in between two VSe_2 layers and the superstructure at the surface is related to the periodicity of the intercalated Cr layer. The experimental results are supported by DFT calculations that suggest that Cr-intercalation is favored over Cr adatoms in bilayer structures.

Our study presents successful incorporation of dissimilar metal atoms into the van der Waals gap of TMDs by post growth intercalation. This opens new opportunities for engineering of layered materials. This intercalation process may be combined with van der Waals epitaxy and thus creates a new direction for modifications of van der Waals heterostructures.

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2D-ThP-7 Quantum Confinement in Topological Semimetal Nano-Platelets, ***Margaret Brown,*** *R. Laing, T. Muratore,* University of Dayton*; K. Burzynski, J. Brown,* Wright Patterson Air Force Base*; J. Corbett,* Miami University*; K. Eyink,* Wright Patterson Air Force Base*; S. Elhamri,* University of Dayton*; A. Reed,* Wright Patterson Air Force Base

Topological insulators (TI) have shown widespread excitement in the development of spintronic devices and quantum computers. Despite their revolutionary properties, the small band gaps of many TIs severely limit their potential applications. Investigations which involve increasing the bandgap are vital in supporting the implementation of this material class. One route to do so uses nano-sized grains of the material to employ quantum confinement. Quantum confinement in TIs increases in bandgap and quantizes the Dirac cone as a function of nano-particle size. Inspired by such, this presentation consists of two parts: nano-platelet growth and resulting bandgap characterization. A study of the topological semimetal, Bi_4Se_3, grown via direct current magnetron sputtering revealed the nucleation process across a variety of growth pressures using atomic force microscopy. All films began as island-type nucleation and transitioned to layered growths at varying transition thicknesses which depend on pressure. During the initial nucleation period, prior to the layering transition, the morphology is composed of many nano-platelets dispersed with nearest neighbor ordering. The sizes of the nano-platelets are controlled by deposition time and growth pressure. Ultra-violet to visible light spectroscopy was used to investigate the dependence of the optical bandgap on the dimensionality of these nano-platelets. Variation of the optical bandgap was observed over a range from 1.55 eV to 2.21 eV with decreasing average platelet volume of 200,000 nm^3 to 30,000 nm^3. Using these data, fine tuning of the nano-platelet bandgaps to meet a range of needs for optical applications becomes possible.

2D-ThP-8 Characterizing the Low-Symmetry Crystallographic Axis in Atomically Thin WTe2 Layers Using Raman Spectroscopy for Spin-Orbit Torque Studies, ***Anh Ramirez,*** *I. Kao, R. Muzzio, J. Katoch, S. Singh,* Carnegie Mellon University, USA

Low-symmetry crystal structure and topological electronic structure in WTe_2, which is a Weyl semimetal candidate, can be used to generate spin current with controllable spin polarization. Spin-orbit torques (SOT) exerted on a nearby magnetic thin film by the spin current in WTe_2, is appealing for an energy efficient field-free magnetization switching[1]. For the field-free SOT switching, it is essential to distinguish the crystallographic orientation in mesoscopic flakes of WTe_2 a so that charge current can be applied along the low-symmetry axis for generating out-of-plane oriented spin currents. We will present our polarized Raman spectroscopic studies on WTe_2 flakes that we use to prepare SOT switching devices. Raman spectra are collected by rotating the polarization of the incident laser for different angles relative to the a-axis of WTe_2. The polarization angle dependence of the Ag Raman peak at 212 cm^{-1} exhibits minimum intensity when the excitation laser polarization is along the straight edge of the WTe_2 flake, which allows us to characterize the crystallographic axis in WTe_2.

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2D-ThP-11 Designing a Green Synthesis Route and a Green Solvent to Exfoliate Graphene for Cost-Efficient Supercapacitors, *S. Kittur, J. Zhang, A. Pangal, I. Agrawal, S. Raj,* ***Abhiram Hanumanchi,*** *N. Sangeneni,* ASDRP

Graphene, the two dimensional counterpart of graphite, is a novel hexagonal lattice structured, single layer sheet of carbon atoms. The material exhibits unique and suitable properties for applications in supercapacitors—notably, high electrical conductivity, lightweight structure, and high tensile strength, The main challenge of producing graphene lies in discovering a process that is green, scalable, and cost-effective. Other processes such as mechanical or electrochemical exfoliation, oxidation/reduction, chemical synthesis, and chemical vapor deposition fall short in at least one of these categories. Instead, our research turns to a more promising method—liquid-phase exfoliation. Refinement of the LPE method included comparisons of bath and probe sonication in their effects on yield. Additionally, we explored the supplementation of magnetic stirring and centrifuging to the process, and the effects of these additions on the end yield. The end yield of graphene was free of trapped oxygen atoms, as confirmed by XRD characterization. Moreover, our experiment did not involve any toxic solvents that pose environmental risks during disposal. Previous research indicates that solvents' properties determine the quality and amount of graphene produced. Solvents with similar surface tensions to graphene are better able to permeate in between the graphite layers during the sonication process. Ethanol in particular is suitable due to its low boiling point, low toxicity, and mix of polar and nonpolar properties. Ethanol's low surface tension in comparison to graphene was remedied by adding water so that the mixture's surface tension was similar to graphene's. We calculated the ratio of water and ethanol to be used based on their surface tensions, which are 73 and 21 mJm-1 respectively. Adding materials like curcumin to the solvent also decreases the amount of defects in graphene, and gives us a better yield. In addition curcumin also acts as a reducing and stabilizing agent, which helps in avoiding agglomeration and keeping the graphene sheets apart. UV-Vis, XRD, and FTIR spectroscopy were used to characterize impurities in the exfoliated graphene. We prepared inks from the exfoliated graphite and performed cyclic voltammetry and galvanostatic charge discharge to test the energy capabilities of graphene electrodes. To further our research, we plan on conducting characterization with Raman spectroscopy and SEM. A green solvent and synthesis process remains desirable in the field of electrochemistry, providing sustainable storage for electricity without a massive loss in yield.

2D-ThP-12 Chemical Vapor Deposition of Large Grain and Continuous Mos$_2$ Layers on Catalyzed SiO$_2$/Si Substrate*, Z. Graham,* ***Matara Indika,*** *M. Williams,* Clark Atlanta University

MoS$_2$ has shown to be remarkable in its electrical and optoelectrical capabilities. Studies exemplify that with its modulating band gap and other properties, it can be useful as an excellent semiconductor material in devices such as field-effect transistors, photodetectors, solar cells. A uniform, continuous, monolayer growth of MoS$_2$ has still been regarded as a challenge in 2-D transition metal dichalcogenide growth. Here in this study, using a conventional CVD (chemical vapor deposition) growth method under particular growth parameters, large-grain and continuous MoS$_2$ layers can be achieved based on the synergistic reaction of precursor and Na2SO$_4$catalysis on a SiO$_2$/Si substrate with no powder transition metal precursors. Experimental studies have proven that rather than the Na interfering with the growth process between molybdenum and sulfur, it does in fact act as a catalyst in this reaction and bonds with the SiO$_2$/Si substrate instead. Confocal laser microscopy, Raman and Photoluminescence techniques will be utilized to study the uniformity/surface morphology, size, thickness, strain, stress, band gap, spin–orbit coupling, etc. of these layers.

Applied Surface Science Division
Room Ballroom A - Session AS-ThP
Applied Surface Science Poster Session

AS-ThP-1 Isolation of Pt Metal Atoms Using a Surface-Catalyzed Covalent Organic Framework*,* ***David Wisman,*** Indiana University Department of Chemistry; NAVSEA Crane*; Y. Bai, S. Tait,* Indiana University Department of Chemistry

Single-site metal centers in heterogeneous catalysts are highly desirable to improve reaction selectivity, due to the uniform active site geometry. It is often advantageous to have a predictable 2-D structure of single-site metal centers, making it necessary to integrate the single-site centers into an ordered array of receptor sites. One way to approach this challenge is through the formation of covalent organic frameworks (COFs). In the work reported here, we utilize a surface-assisted dehalogenation reaction of 1, 3, 5–tris(4-bromophenyl)benzene (**TBB**) to form a 2-D covalent organic framework on single-crystal metal surfaces. Following successful formation of the 2-D framework on the surface, favorable binding sites for metal catalysts (platinum) are formed by depositing 1, 10-phenathraline-5, 6-dione (**PDO**) on the surface. **PDO** becomes confined within the porous COF and is then able to stabilize vapor deposited metal and single atom sites. X-ray photoelectron spectroscopy confirms the oxidation of the platinum metal when deposited with **PDO** molecules, while scanning tunneling microscopy confirms the confinement of **PDO** within the pores, and the absence of any external 1-D Pt:**PDO** chains. The highly predictable nature of the covalent organic framework chemistry makes this an exciting result for single-site metal center formation.

AS-ThP-2 In situ Spectroscopic Evaluation of the Aging Mechanisms of Molybdenum Disulfide*,* ***Robert Chrostowski,*** University of Texas at Austin*; J. Curry, M. Dugger,* Sandia National Lab*; F. Mangolini,* University of Texas at Austin

Molybdenum disulfide (MoS2) is a lamellar transition metal dichalcogenide extensively used as a solid lubricant in the aerospace industry due to its beneficial lubricating properties (i.e., low friction) in vacuum. Unfortunately, exposure to environmental contaminants, believed to be primarily oxygen and water, degrades the tribological performance of MoS2 in a process known as "aging". While aging of MoS2 coatings has been recognized as an important engineering problem occurring even in high-vacuum, the underpinning mechanisms are still poorly understood. Developing a fundamental understanding of chemical processes occurring in MoS2 and their kinetics upon exposure to different gases can provide guidance for developing novel approaches to prevent and/or reverse aging of MoS2 coatings.

Here, we employ an in situ surface-analytical approach, based on the combined use of time-of-flight secondary ion mass spectrometry (ToF-SIMS) and X-ray photoelectron spectroscopy (XPS), to evaluate and quantify the surface chemical changes occurring upon aging MoS2 in aerobic conditions. Additionally, in situ annealing experiments of MoS2 samples inside the XPS chamber were carried out to evaluate the effect of annealing before and after aging on the surface chemical processes occurring inside and outside wear tracks upon aging. Finally, to identify the relative contribution of oxygen and water to the aging process, MoS2 samples were exposed to deuterium oxide (D2O) and oxygen-18 (18O) in the ToF-SIMS chamber. The subsequent ToF-SIMS analyses provided evidence for the high diffusivity of water in MoS2, and, especially, in tribologically-stressed regions.

The results of these investigations, providing novel insights into the relative contribution of oxygen and water to aging of MoS2 coatings and the effect of tribologically-induced structural variations on the transport of water in the near-surface regions of MoS2, add significantly to the understanding of the mechanisms underlying the aging process.

AS-ThP-4 Stm Investigations of Self-Assembly of Proline*,* ***Benjamin Heiner,*** *A. Pittsford, S. Kandel,* University of Notre Dame

Scanning tunneling microscopy, through the observation of molecular clusters and monolayers on surfaces, provides direct experimental evidence as to how intermolecular interactions result in the self-assembly of extended structures. A detailed understanding of the interplay of interactions will result in improved understanding and prediction of the behavior of self-assembling systems, with implications in a wide range of disciplines ranging from crystal engineering to supramolecular chemistry to protein secondary and tertiary structure. We present experimental results on the self-assembly of proline, as well as the results from computational modeling. Pulse deposition of d-proline on Au(111) reveals that it forms dimer or catamer chains and pentamer clusters. The dimer structures are chiral, as would be expected from an enantiopure adsorbate; however, the pentamers on the surface appear racemically mixed. Comparison of self-assembled structures to related molecules reveals similar behavior for proline, indole-2-carboxylic acid, and indoline-2-carboxylic acid, but substantial differences are observed for pyrrole-2-carboxylic acid.

AS-ThP-5 Efforts to Improve XPS Analysis Quality in an Era of Increasingly Diverse Uses and Users*,* ***Don Baer,*** Pacific Northwest National Laboratory*; J. Watts,* University of Surrey, U.K.*; A. Herrera-Gomez,* CINVESTAV-Unidad Queretaro, Mexico*; M. Linford, G. Major,* Brigham Young University

Use of XPS in publications continues to increase exponentially but anecdotal reports and systematic analyses show a growing presence of significantly flawed data and analyses. Examination of six months of XPS data in three journals found more than a quarter of the data presented to be highly flawed, often leading to incorrect conclusions. Recognition of this problem within the surface analysis community has increased with recognition that inexperienced users and increased use of XPS outside the surface analysis community contribute to the problem. Several efforts have been initiated to address the problem. This poster will identify some of the specific problems and describe some of the community efforts intended to address them. Challenges associated with reliable repeatable XPS measurements were recognized at the advent of commercial instrumentation and led to the formation of relevant ASTM and ISO standards committees. Recent efforts to address problems found in the literature include, review papers and tutorials including collection of papers on reproducibility with a focus on XPS in the Journal of Vacuum Science and Technology A (JVSTA), websites containing and summarizing useful information, implementation of expert systems to assist the collection and analysis, advanced software tools, and online forums that can enable community interactions to assist analysts. The poster focuses on evolving efforts to address three specific issues: i) incomplete data and analysis reporting, ii) the need for bite sized versions of important information for non-experts and iii) the high rate of peak fitting problems. Examination of XPS containing papers finds that information important for reproducible XPS results is often very incomplete. Approaches to develop, distribute, and encourage use of essential analysis information are being explored. To address the shorter attention spans of many in the age of online media and social networks papers to provide incremental bites of useful information are being developed for a series of paper to appear *Surface and Interface Analysis*. Multiple efforts are underway to address the high rate of problems associated with photoelectron peak fitting. These include guides to peak fitting, guides to peak identification and fitting for specific elements, and development of a peak fitting social network designed to connect new and experienced XPS users. In addition, development of a second JVSTA collection of Reproducibility Challenges and Solutions papers is under way.

AS-ThP-6 Metrology Developments in XPS and HAXPES*, **David Cant**, B. Reed, A. Shard,* National Physical Laboratory, UK

X-ray photoelectron spectroscopy (XPS) is a highly quantitative and surface sensitive technique for analysis of the chemical composition of a given sample. However, it is important that the data obtained during a photoemission experiment is interpreted correctly – both instrumental and sample-related factors must be accounted for to obtain a quantitative understanding of the sample composition. It is necessary to know the *energy-dependent spectrometer response function* ('transmission function') of the XPS instrument, as well as the *sample-dependent relative sensitivity factors* (RSFs) which account for the differences in emitted electron intensities for each peak.

In a recent VAMAS interlaboratory study, the huge variability of transmission functions between different laboratories and instruments has been demonstrated, underlining the need for an ISO standard on XPS intensity calibration which is now being developed under the auspices of ISO TC201 “Surface Chemical Analysis”. Here we present instrument geometry-corrected reference spectra of low-density polyethylene (LDPE) for Al Kα instruments which are traceable to gold, silver, and copper reference spectra from the National Physical Laboratory (NPL). Sensitivity factors are required to account for differences in the intensity of emitted electrons from different materials within a sample. Such differences arise due to several factors, including the photoionisation cross-section; electron kinetic-energy-dependent variations in transport through a material; and the anisotropic emission of excited electrons. Theoretically determined sensitivity factors, such as the NPL AMRSFs for Al and Mg anode instruments,are commonly used.

For hard x-ray photoelectron spectroscopy (HAXPES), photoionisation cross-sections decrease significantly as photon energy increases, and anisotropy effects become more complex due to the increased contribution of non-dipolar effects. It is therefore increasingly important that a careful consideration be given to the estimation of RSFs. This is further complicated by the multiple photon energies and instrument geometries available in commercially available HAXPES instrumentation. Here we present a set of formulae, derived from fitting of theoretical database values, which allow the estimation of AMRSFs for instruments using any photon energy in the range 1.5 keV - 10 keV, with any instrument geometry. A few instrument geometries in which X-rays are polarised are insensitive to angular emission effects, and these are highlighted in this work.

AS-ThP-7 Advances in Automated XPS Analysis – from Data to Answers*, S. Coultas, J. Counsell,* Kratos Analytical Limited, UK*; C. Moffitt,* Kratos Analytical Inc*; K. Good, K. Macak, **Christopher Blomfield**,* Kratos Analytical Limited, UK

XPS has become a mainstay of the suite of analytical tools available for characterisation of new materials and processes.It would be fair to say that XPS instrumentation is now viewed as a “tool” by many users and the expectation is therefore that results are automatically produced.Here we discuss the latest improvements and advancements which provide not just data but results and answers.We look at improving peak identification from unknown samples and automatic region spectral acquisitions.In addition, we show how known samples can be quickly and efficiently acquired and processed to provide comparison results for QA or trend analysis.

AS-ThP-10 The Role of Artificial Intelligence in Minimizing Analysis Errors, Illustrated with EXAFS, Nanoindentation, and Core Level Photoemission*, **Jeff Terry**,* Illinois Institute of Technology

We have developed artificial intelligence based methodology that can be utilized to reliably analyze experimental results from Extended X-ray Absorption Fine Structure (EXAFS) measurements. This development will help to address the reproducibility problems that slow research progress and inhibit effective tech transfer and manufacturing innovation in these scientific disciplines. A machine learning approach was applied to the analysis of extended X-ray absorption fine structure (EXAFS) spectroscopy measurements collected using a synchrotron radiation facility. Specifically, a genetic algorithm was developed for fitting of the measured spectra to extract the relevant structural parameters. The current approach relies on a human analyst to suggest a potential set of chemical compounds in the form of feff.inp input files that may be present. The algorithm then attempts to determine the best structural paths from these compounds that are present in the experimental measurement. The automated analysis looks for the primary EXAFS path contributors from the potential compounds. It calculates a goodness of fit value that can be used to identify the chemical moieties present. The analysis package is called EXAFS Neo and is open source written in Python. It requires the use of Larch and Feff for calculating the initial EXAFS paths. We have recently extended the code to make use of Feff8.5lite so it can calculate the paths needed for populating the analysis from within the EXAFS Neo package. The code base has been expanded for the analysis of nanoindentation data and simple x-ray photoelectron spectroscopy measurements. The publication describing the analysis package and where to obtain the software can be downloaded at: https://doi.org/10.1016/j.apsusc.2021.149059 or by contacting the speaker.

AS-ThP-11 X-ray Photoelectron Spectroscopy of Polymer Electrolyte Membrane Fuel Cell Components*, **Maxim Shepherd**, S. Pylypenko,* Colorado School of Mines

Development of sustainable technologies that produce energy are extremely important to reduce the environmental impacts of current technologies. Proton exchange membrane fuel cells (PEMFCs) generate clean energy using hydrogen and oxygen with water as the main byproduct. The state-of-the-art catalyst for the oxygen reduction reaction occurring at the cathode is based on Pt nanoparticles dispersed on carbon support (Pt/Carbon). The cathode catalyst layer has a major influence on the overall cost of a PEMFC due to the loading of platinum that is needed to achieve a reasonable power density. Optimization of the catalyst layers to achieve the most efficient distribution of the ionomer coating which directly effects the mass transport and device efficiency, is one of the current needs especially for catalysts layers produced using scalable routes. Furthermore, there is a general lack of understanding about how the catalyst support, catalyst, and ionomer interact with one another on a molecular scale. This work utilizes X-ray Photoelectron Spectroscopy (XPS), a highly surface sensitive technique to characterize elemental and chemical speciation of the catalyst layers. XPS is a very common technique to study catalyst but has not been widely applied to investigate catalyst layers.This poster will provide a general background on sample preparation, and data acquisition and analysis of catalysts and catalysts layers made with platinum on High Surface Area Carbon (HSC) catalyst, including findings related to Nafion ionomer degradation. Furthermore, this poster will present comparison of chemistry of the catalyst before and after incorporation into catalyst layer, and will discuss composition of catalyst layers as a function of ionomer loading.

AS-ThP-12 Nanoscale Surface Sensitive Chemical Imaging of Additive Manufacturing Materials*, **Ashley Maloney**, K. Artyushkova,* Physical Electronics USA*; O. Renault, E. De Vito,* CEA/LETI-University Grenoble Alpes, France

Additive manufacturing is an ever-growing area of research interest that depends upon the high quality of precursor materials in order to achieve a robust final printed product. In this work, an alloy powder material of CuCrZr used in the laser-powder bed diffusion process of 3D printing will be analyzed for grain boundary diffusion and for chemical variation among different particle sizes. Recent advances in Auger Electron Spectroscopy, including *in situ* FIB capabilities, put AES at the forefront of surface analysis techniques with respect to characterization of such defects on the nanoscale. The quantitative elemental information AES provides from solid surfaces combined with FIB tomography allows for *in situ* cross-sectioning and subsequent elemental characterization of the CuCrZr powder particles. The variation of chemistry across different sized particles will also be assessed via quantitative chemical analysis using XPS.

In this work, CuCrZr alloy powder particles were cross-sectioned and analyzed using a PHI 710 scanning Auger nanoprobe equipped with a 25kV Schottky field emission electron gun and a coaxial Cylindrical Mirror Analyzer (CMA). We demonstrate the use of AES in conjunction with a focused ion beam (FIB) to produce site-specific imaging of grain boundary diffusion within the alloy.

AS-ThP-13 Data Reporting in XPS: A Consistent Lack of Information*, **Max Clark**, G. Major, M. Linford,* Brigham Young University

X-ray photoelectron spectroscopy (XPS) is widely used to probe the top 10 nm of materials. It is based on the photoelectric effect. Spectra acquired in XPS typically require peak fitting. To properly peak fit, various mathematical functions, including the background and peak shapes, are used. Additionally, different experimental conditions typically change the types of peaks that are required for a fit. We have surveyed the XPS reporting from 2021 papers in three major journals. About 900 papers were surveyed. Only 70% listed the XPS instrument that was used. Among publications with fitted XPS data, over 90% did not indicate the line shape(s) used and over 35% did not indicate the background used. In this presentation, we provide information on other aspects of reporting as well. To improve the reporting in the literature, which should improve the reproducibility of studies, we recommend that (at a minimum) the following be reported:

62. The manufacturer and model number of the photoelectron spectrometer
63. The X-ray anode and energy (for example, in conventional XPS, Mg K⍰ or Al K⍰ with energies of 1253.6 or 1486.6 eV, respectively)
64. The type of source: non-monochromatic or monochromatized
65. The X-ray power and spot size
66. The photon energy used in the measurement, along with energy resolution
67. The vacuum level during the analysis Additionally, information about the line shape(s), fitting program, peak positions, and background should also be included if fitting data.

AS-ThP-14 Electrochemical Flow Cell for Surface and Interface Analysis Cluster*, **Soniya Gahlawat,*** CEST Kompetenzzentrum für elektrochemische Oberflächentechnologie GmbH, Austria*; M. Valtiner,* TU Wien/IAP, CEST Kompetenzzentrum für elektrochemische Oberflächentechnologie GmbH, Austria

Electrochemistry plays a pivotal role in scientific and technological advancements. In order to achieve the circular carbon neutral economy goals, we need to advance our infrastructure to study electrochemical processes such as hydrogen production, batteries, fuel cells, recycling, and corrosion. The common feature in all these processes are interface reactions and the key to further development is improving the understanding of these phenomena.

In fundamental research, we have seen increasing use of classical Ultra-High Vacuum (UHV) analysis techniques at higher pressures, although the pressure range is still well below atmospheric conditions and even more so below operating conditions of any real-world electrochemical device.[1] Therefore, we decided to mimic the real operating conditions for electrochemical devices and combined with UHV surface and interface analysis techniques. We integrate the electrochemistry into a UHV system for quasi-operando analysis to explore the energy storage and conversion research areas at nanoscale.

The major challenge with operando and in-situ clusters is to have an ideal electrochemical flow cell suitable for studying the solid/liquid interface dynamics. Most of the cells with easy transfer of working electrode have poor electrode geometries, which results in high ohmic resistance. Additionally, it is pertinent to prevent the presence of organic impurities in the cell as they may get adsorb at the surface and obstruct the surface-interface analysis. We have initiated the development of our experimental setup based on a cell designed by Olaf Brummel[2] and tried to overcome the above-mentioned limitations. To avoid the glass corrosion, the lower part of cell is designed with Teflon and further the geometry of the cell is modified in a unique way. I will present my initial results in this direction as well as an overview of electrochemical surface and interface analysis cluster being developed at TU Wien.

References:

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AS-ThP-15 Optical Measurements of Temperature Driven Phase Change in Doped Niobium Oxides for Neuromorphic Computing Applications*, **James Michels**, Z. Robinson, V. Daviero,* State University of New York College at Brockport*; K. Beckmann, N. Cady,* SUNY Polytechnic Institute, Albany

Significant research has focused on low-power stochastic devices built from memristive materials. These devices foster ‘neuromorphic’ approaches to computational efficiency enhancement in merged biomimetic and CMOS architectures. Niobium dioxide has volatile memristive properties that include a phase change from an insulating to a conductive state at temperatures above around 800C. This phase change makes it an ideal candidate for future neuromorphic electronics. An ultra-high vacuum technique for measuring the effect of dopants on the phase change has been built, and relies on *in situ* infrared spectroscopy to assess the effect of the phase change on optical reflection and transmission. Further, changes in the macroscopic optical absorption properties of titanium doped NbO_2 are presented as a function of temperature and optical wavelength. The results reveal an interesting optical transmission behavior in a localized temperature range in contrast to its overall decrease with increasing temperature. The latter may provide modulation capabilities for memristive devices.

AS-ThP-16 Laser Surface Melting to Mitigate Intergranular Corrosion of Sensitized AA 5083*, **Md Sojib Hossain,*** University of Virginia, USA, Bangladesh*; J. Skelton,* University of Virginia*; W. Moffat, A. Wang, G. Lu, J. Fitz-Gerald,* University of Virginia, USA

The precipitation of an anodic Mg-rich phase in 5xxx series aluminum alloys causes them to become sensitized and highly susceptible to corrosion, especially when used in marine-based applications. Heat treatments (>240°C) can dissolve the secondary phases back into the matrix but are unrealistic for service components. In this study, laser surface melting (LSM) is used to reverse the sensitization at the alloy’s surface. An excimer ns-pulsed laser was employed at a fluence of 1.5 J/cm 2 to rapidly melt and solidify the surface of highly sensitized AA5083 samples. Characterization of the composition, roughness, and corrosion resistance of these samples were performed to achieve a holistic understanding of how the alloy surface changes after laser melting. Results show that laser processing decreased the open circuit potential from -780 mV to -980 mV (vs. SCE) due to surface homogenization and dissolution of secondary phases, which contribute to micro-galvanic corrosion. A reduction in the corrosion rate was attributed to the dissolution of anodic precipitates into the solid aluminum solution within the melted region, approximately 7 um deep beneath the surface. This work illustrates the efficacy of using LSM to reverse the sensitization of Al-Mg alloys, leading the way toward a method of restoring the original corrosion resistance of sensitized in-service material

AS-ThP-17 Chemistry and Mechanism of Two-Dimensional Transition Metal Carbide and Nitride Mxene Synthesis*, **Mark Anayee**, R. Wang, Y. Gogotsi,* Drexel University

MXenes comprise a family of two-dimensional carbides and nitrides that has grown to encompass numerous structures and compositions – >30 single transition metal MXenes with a near infinite number of solid solutions ranging in thickness depending on the number of atomic layers, from 5-11. MXenes are promising for a variety of applications ranging from electrodes for energy storage to wireless communication, optoelectronics, and medicine because of their high electrical conductivity, redox-active surfaces, plasmonic behavior, and other attractive properties. MXenes are typically derived *via* topochemical etching of atomically thick layers from precursor layered MAX phases using corrosive halogenated aqueous or vapor etchants. Knowledge of the reaction mechanism and process kinetics are of fundamental importance for the synthesis and property control of MXenes. Prediction of the optimal synthesis approaches will facilitate new MXene composition discovery and prediction of optimal processing time as a function of various parameters will also facilitate scaling up the wet chemical synthesis of MXenes for industrial use. Despite their importance, such studies have been challenging because of the atomic thickness of the A-element layers being etched and the aggressive etchants that hinder in situ studies. Herein, we investigate the defects in the metal and carbon site in the parent MAX phase using ex situ photoemission spectroscopy and mass spectrometry to understand how MXenes develop from MAX phases.

Moreover, we investigate the effect of such defects and MAX structure and chemistry influence the etching reaction mechanism through in situ optical profilometry and Raman spectroscopy of single MAX particles to monitor the structural and chemical transformation. Through these methods, we gain fundamental understandings of atomic etching mechanism and kinetics for layered materials and how the reaction starts, proceeds, and finishes.

AS-ThP-19 Multilayer Method Modification for the Quantitative Chemical Composition Analysis on Initial Oxidation of Nickel*, D. Guzmán Bucio, G. Gómez Sosa, D. Cabrera German , M. Bravo Sánchez, J. Torres Ochoa, O. Cortazar Martínez , A. Carmona Carmona,* ***Alberto Herrera Gómez****, M. Mayorga-Garay,* CINVESTAV-Unidad Queretaro, Mexico

Peak-fitting of the Ni 2p core-level from metallic nickel and its oxides is challenging due to the high asymmetry of the main peak, the complex multiplet structure, and the intense Shirley-type background. This work presents X-ray photoelectron spectra acquired from a clean metallic Ni film (sublimated on Si [001]). These are analyzed with two approaches that account for the apparent asymmetry of the main photoemission line: one being the use of the double Lorentzian asymmetric line shape; the other, a set of symmetric peaks. Both approaches lead to excellent fits with undistinguishable peak envelopes and backgrounds; however, they lead to different sets of previously unreported low-intensity satellites. The application of the Block Approach to the analysis of the partially oxidized Ni spectra allowed for the robust identification of five doublets corresponding to the oxide. It is remarkable that the sum of these oxide peaks closely reproduces the Ni^{3+} spectra, which is consistent with the assessed composition ($Ni_2O_{3.1\pm0.3}$). The strong overlap and shape similarity of the Ni0 $L_3M_{45}M_{45}$ Auger structure with that of the Ni^{3+} strongly suggests that the Auger Parameter modified does not provide additional information to that provided by the binding energy shift of the 2p core level. The latter is in contrast to the claims made by other specialists. The angular dependence of the peak intensities is not consistent with a simple layer oxidation mechanism but with the formation of oxide regions protruding deeper into the film. The existence of regions with protrusions might depend on the grain orientation. For the first time in the history of X-Ray Photoelectron Spectroscopy, in the analysis of the surface chemical composition and the morphology, the uncertainty propagation methods were applied considering the covariance between the parameters of the depth profile parameters and those of the chemical composition.

Electronic Materials and Photonics Division
Room Ballroom A - Session EM-ThP
Electronic Materials and Photonics Poster Session

EM-ThP-2 Synthesis and Characterization of $Pb(In_{1/2}Nb_{1/2}O_3)$-$Pb(Mg_{1/3}Nb_{2/3}O_3)$-$PbTiO_3$ Thin Films Grown by Pulsed Laser Deposition*,* ***Da-Ren Liu****,* Taiwan Instrument Research Institute, National Applied Research Laboratories, Taiwan

Because of their extraordinary large electromechanical coupling coefficient and piezoelectric coefficient, relaxor-based ferroelectric crystals $Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ (PMN–PT) and $Pb(In_{1/2}Nb_{1/2})O_3$–$Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ (PIN–PMN–PT) with morphotropic phase boundary (MPB) have attracted extensive attention. They also become important materials in the fabrication of high-performance electromechanical devices including transducers, actuators and sensors. However, with its concentration of PT near the morphotropic phase boundary region, the PIN–PMN–PT not only has similar piezoelectric performance to that of the binary PMN–PT but also possesses higher phase transition temperature and coercive field. In this study, highly textured thin films of the PIN–PMN–PT were grown on $SrTiO_3$ substrates by Nd:YAG pulsed laser deposition(PLD). According to the results of glancing-angle x-ray powder diffraction (GAXRD), the PIN-PMN-PT films are polycrystalline with a preferential growth direction.The thickness and roughness of the films were characterized by grazing-incidence x-ray reflectivity (GIXR), and the piezoelectric constant d_{33} was measured by the piezoelectric force microscopy(PFM).The complex refractive indices were measured in the range from 1.5 to 4.2 eV by spectroscopic ellipsometry (SE). The average oscillator strength and its associated wavelength were estimated by using a Sellmeier-type dispersion equation.

EM-ThP-3 The Study of Magnetic and Electrical Properties of Co Spin Crossover Molecule Thin Films*,* ***Jared Phillips****, S. Yazdani,* Indiana University-Purdue University-Indianapolis*; T. Ekanayaka, E. Mishra,* University of Nebraska*; J. Soruco,* Indiana University-Purdue University-Indianapolis*; A. N'Diaye,* Advanced Light Source, Lawrence Berkeley National Laboratory*; P. Wang,* University of Florida*; M. Shatruk,* Florida State University*; P. Dowben,* University of Nebraska*; R. Cheng,* Indiana University-Purdue University-Indianapolis

Spin crossover complexes (SCO) exhibit a bistability, and can be switched between a low spin and a high spin state via a wide range of external stimuli, including temperature, irradiation and electric field. Accompanying the change in spin state there are often dramatic changes in other physical properties, such as color, magnetic moment, and conductance. A recently synthesized valence tautomeric SCO molecule, $[Co(SQ)_2(3\text{-}tpp)_2]$, displays a bistable conductance with a noteworthy low resistance in the high state, making this SCO molecule particularly intriguing for organic device applications. In this work, we detail the temperature, light and voltage dependent conductance properties in the context of the spin state and magnetic field dependent properties of this molecule drawing from results acquired from X-ray absorption spectroscopy (XAS), X-ray magnetic circular dichroism (XMCD), and electronic transport studies. Conductance properties depend on the molecular thin film so we will also discuss the methods and the techniques used to fabricate high quality thin films and the challenges to better thin film growth.

EM-ThP-5 Multi-Frame Gated X-Ray Imager (MGXI) for Fast Hard X-Ray Imaging*,* ***Mary Ann Mort****, C. Hunt,* University of California at Davis*; A. Carpenter,* Lawrence Livermore National Laboratory

The proposed multi-frame gated x-ray imager (MGXI) is a fast, hard x-ray imaging diagnostic for use in inertial confinement fusion (ICF) and high energy density (HED) experiments at the National Ignition Facility (NIF), such as Compton radiography and hot spot imaging. Individual MGXI component testing is happening in phases at Lawrence Livermore National Lab (LLNL) and the UC Davis Vacuum Microelectronics Lab. The Icarus2 hCMOS sensor was tested with a class 1 laser in both the high speed timing (HST) and manual shutter testing (MST) modes. Microchannel plates (MCPs) will be tested under vacuum with an electron gun and a simple photodiode array. MGXI has goals to image 10-100keV x-rays with 100-1000 ps temporal resolution in 2-8 frames and >5% detector quantum efficiency (DQE).

Fundamental Discoveries in Heterogeneous Catalysis Focus Topic
Room Ballroom A - Session HC-ThP
Heterogenous Catalysis Poster Session

HC-ThP-2 Facet-Dependent Strong Metal-Support Interaction of Pt Nanoparticles on Morphology Controlled Cu_2O Under CO Oxidation*,* ***Seunghwa Hong****, D. Kim,* Korea Advanced Institute of Science and Technology (KAIST) & Institute for Basic Science (IBS), Republic of Korea*; Y. Song,* Korea Advanced Institute of Science and Technology, Republic of Korea*; K. Kim,* Pohang Accelerator Laboratory (PAL), Republic of Korea*; J. Park,* Korea Advanced Institute of Science and Technology (KAIST) & Institute for Basic Science (IBS), Republic of Korea

The strong metal-support interaction (SMSI), the interaction between metal nanoparticle and metal-oxide support, plays a central part in the catalytic behavior of catalysts, due to synergistic effects on reactivity at the metal-oxide interface. Thus, a fundamental understanding of SMSI in realistic conditions is important to the development of high-performance catalysts. However, direct investigation of SMSI is challenging, due to the structural complexity of the heterogeneous catalysts. Fac-et-controlled metal-oxide supports, such as Cu_2O, are excellent candidates for studying the SMSI at the metal and metal-oxide interface, since they possess well-defined surface structure. Furthermore, utilizing operando techniques enables in-depth characterization of the interactions at metal and metal-oxide support interfaces with a molecular level in a realistic environment.

Herein, we investigated facet-dependent SMSI at Pt nanoparticles supported on cubic and octahedral Cu_2O using surface-sensitive operando techniques. The catalytic measurement revealed facet-dependent CO oxidation activity for Pt/cubic Cu_2O and Pt/octahedral Cu_2O catalysts.

Furthermore, the results of in-situ ambient pressure X-ray photoelectron spectroscopy and diffuse reflectance FT-IR spectroscopy indicate that the surface changes during the reaction depend on the facet of the support, leading to different catalytic performances. This investigation of the facet-dependent sur-face changes that significantly influence reactivity provides insight into designing high-performance catalysts via engineering the interface interaction.

**HC-ThP-3 Investigation of Strong metal-support Interaction at the Pt-CoO interface Formed on Pt-Co Bimetallic Nanoparticles*, Yejin Song*, *D. Kim, S. Hong,* Korea Advanced Institute of Science and Technology (KAIST) & Institute for Basic Science (IBS), Republic of Korea*; K. Kim,* Pohang Accelerator Laboratory (PAL), Republic of Korea*; J. Park,* Korea Advanced Institute of Science and Technology (KAIST) & Institute for Basic Science (IBS), Republic of Korea

Bimetallic nanoparticles are important catalysts in heterogeneous catalysis; due to the bimetallic synergistic effect, they show higher catalytic performance than monometallic nanoparticles. Pt, a widely used catalyst, is known to alloy well with 3d transition metals (TM, e.g., Ni, Fe, Cu, and Co). In Pt-3d TM bimetallic systems, surface restructuring occurs in a variety of environments. Under oxidation conditions, Co atoms in Pt-Co nanoparticles emerged onto the surface, forming a CoO layer. Moreover, the interface between Pt and CoO enhanced catalytic activity for the Pt-Co bimetallic nanoparticle. This catalytic improvement could be explained by the strong metal-support interaction (SMSI) at the Pt-3d TM oxide interface, from the surface restructuring.

In this study, we investigated the role of the Pt-CoO interface in Pt-Co bimetallic nanoparticles during CO oxidation with surface analysis. Pt-Co nanoparticles of 4 nm were synthesized by the co-reduction method with polyvinylpyrrolidone (PVP) as a capping agent. Pt-Co bimetallic nanoparticles were supported on SiO_2 to be applied to the CO oxidation reaction. Pt-Co bimetallic catalysts exhibited higher catalytic activity than monometallic catalysts. To verify the SMSI effect at the interface of Pt-CoO in Pt-Co bimetallic nanoparticles, *operando* surface analysis, ambient pressure X-ray photoelectron spectroscopy and in-situ diffuse reflectance infrared Fourier-transform spectroscopy, were used. This study demonstrates that reaction-driven metal-oxide interface is a key factor in boosting catalytic activity.

HC-ThP-4 Effusive Molecular Beam Study of CH_4 Dissociative Chemisorption on Rh(111): The Remarkable Activity of Step Sites and Extrapolation to Catalytic Rh Films at Temperatures where Tunneling Dominates*, Xingyu Wang*, *I. Harrison,* University of Virginia

Effusive molecular beam experiments were used to measure CH_4 dissociative sticking coefficients, $S(T_g, T_s ;J)$ on a Rh(111) crystal, for which the impinging gas temperature, T_g, and surface temperature, T_s, could be independently varied, along with the angle of incidence, J, of the impinging gas. The 500 – 900 K temperature range explored is relevant to heterogeneous catalytic processes such as methane partial oxidation. A dynamically biased precursor mediated microcanonical trapping (PMMT) model of dissociative chemisorption was used to analyze the experimental results. Modelling indicates that the enhanced reactivity of step sites is not promptly poisoned on Rh(111) but rather contributes substantially to the reactivity even as high coverages of carbon accumulate at the surface. Threshold energies for dissociative chemisorption on the terraces and steps sites were optimally modeled as 74.3 kJ/mol and 36.7 kJ/mol. Translations parallel to the surface and rotations were treated as spectator degrees of freedoms. The efficacy of vibrational energy to promote reactivity relative to normal translational energy was h_n=0.55 and one surface oscillator participated in energy exchange within the collisionally formed precursor complexes. A two-channel Arrhenius model restricted to only the thermal dissociative sticking coefficient measured along the direction of surface normal, $S_n(T=T_g=T_s)$, yielded apparent activation energies of 70.6 and 25.5 kJ/mol which could be attributed to terrace and step sites, respectively. PMMT modeling of the step site reactivity on Rh(111) could be extrapolated to replicate the thermal dissociative sticking coefficient of the "defect dominated" Rh film surfaces measured by Ehrlich at temperatures in the 250 -350 K range where much of the elevated kinetic isotope effect (9 to 15) could be attributed to quantum mechanical tunneling through the reactive barrier.

HC-ThP-5 Adsorption and Decomposition of Zirconium Tetrahydroborate on Pd(111)*, Ravi Ranjan*, *M. Trenary,* University of Illinois - Chicago

Zirconium tetrahydroborate, $Zr(BH_4)_4$, is a volatile compound that has been widely used as a single-source precursor to grow carbon-free thin films of zirconium diboride by chemical vapor deposition (CVD). However, the basic surface chemistry of this compound that underlies the CVD process is largely unknown. We studied the adsorption and decomposition of $Zr(BH_4)_4$ on a Pd(111) surface with reflection absorption infrared spectroscopy (RAIRS), temperature-programmed desorption (TPD), and X-ray photoelectron spectroscopy (XPS). Palladium was chosen as the substrate as it is a good dehydrogenation catalyst. The compound was synthesized using literature methods. It was dosed onto the Pd(111) surface using standard gas-handling methods. After exposing Pd(111) at 90 K to $Zr(BH_4)_4$(g), a RAIR spectrum was obtained that closely matched that of the pure compound, indicating that it adsorbs without dissociation at 90 K. However, upon heating to 200 K the RAIR spectrum undergoes dramatic changes indicating that a new surface species is formed that retains B–H bonds, as indicated by a B–H stretch peak at 2540 cm^{-1}. This surface species is tentatively identified as either BH_4 or BH_3 and is stable up to 300 K. Both H_2 and B_2H_6 desorb from the surface at around 175 K as observed with TPD. The decomposition of the BH_x intermediate is revealed by additional H_2 desorption peaks at 325 K and 425 K. Results obtained with XPS suggest that adsorbing $Zr(BH_4)_4$ at low temperature and then annealing does not produce ZrB_2, but instead leaves only Zr on the surface.

HC-ThP-6 Preliminary Studies of RhCu Single-Atom Alloys Using Molecular Beams*, Laurin Joseph*, *M. Powers, A. Utz,* Tufts University

A new class of heterogeneous catalysts called single-atom alloys (SAAs) combine single, isolated atoms of expensive catalytically active metals alloyed into less expensive base metals. These materials have been shown to have greater selectivity and activity relative to conventional catalysts. To date, detailed surface science studies of these materials have been limited to relatively low-barrier reactions. This work will extend the range of detailed mechanistic studies of these promising new materials to higher barrier reactions, including C-H activation. More specifically, our study focuses on the reaction of methane over a RhCu SAA catalyst. This system has been studied using reflection absorption infrared spectroscopy, temperature programmed desorption, and scanning tunneling microscopy previously.[1,2] Our lab will use supersonic molecular beam experiments to learn more about the energetic barriers and kinetics of this reaction. Presented here will be preliminary findings of these experiments as well as an explanation of the modifications made to our apparatus to make the RhCu surface.

1. Hannagan, R. T. et al. *ChemCatChem* **12**, 488–493 (2020).

2. Hannagan, R. T. et al. *Science* **372**, 1444–1447 (2021).

HC-ThP-8 Characterization of a Pt/Cu(111) Single Atom Alloy using CO-RAIRS and CO-TPD*, David Molina*, *M. Trenary,* University of Illinois - Chicago

A combination of reflection absorption infrared spectroscopy (RAIRS), temperature programmed desorption (TPD) and Auger electron spectroscopy (AES) were used to characterize a Pt/Cu(111) single metal alloy (SAA). Carbon monoxide was used as a probing molecule to detect Pt sites in diluted alloys, down to 0.1% Pt/Cu(111) concentrations. CO-TPD spectra for known high concentrations of Pt, quantified by the ratio of the 237 MNN Pt and 920 LMM Cu Auger signals, were used for calibration for samples with Pt concentrations below the AES limit of detection. Initial RAIR spectra of CO saturated diluted alloys at 90 K have shown a signal at 2046 cm^{-1} which is overlapped with the 2078 cm^{-1} CO stretch on Cu(111) on top sites. Annealing at 180 K, above the desorption temperature of CO from Cu(111), and recooling to 90 K clearly show the 2046 cm^{-1} peak. Corresponding TPD spectra have shown desorption of CO at 345 K from the Pt/Cu(111) dilute alloys, in agreement with a previous study of CO desorption from single atom Pt sites on Cu(111). Room temperature RAIR spectra of CO on Pt/Cu(111) alloys with less than 1% Pt concentration have also shown only one vibration at 2046 cm^{-1}, assigned to CO on top of single Pt atoms. Annealing to 500 K starts diffusion of Pt to the bulk, as previously observed in Pt/Cu alloy studies.

HC-ThP-9 Surface Chemistry of Acrolein and its Hydrogenation Products on Cu(111) and Single Atom Alloy Pd-Cu(111)*, Arephin Islam*, *D. Molina, M. Trenary,* University of Illinois - Chicago

Adsorption properties and surface chemistry of acrolein and its hydrogenation products propanal, 1-propanol, and 2-propenol on Cu(111) and Pd-Cu(111) single atom alloy surfaces were studied by polarization-dependent reflection absorption infrared spectroscopy (PD-RAIRS) and temperature-programmed desorption (TPD). The experimental RAIR spectra were obtained by adsorbing multilayers of each molecule at 85 K and then annealing the surface up to 200 K to desorb the multilayer and produce the most stable monolayer structure on both surfaces. Each molecule adsorbs weakly to the surface and desorbs without reaction at temperatures below 200 K. Several TPD spectra were collected following adsorption at 85 K using similar coverages as those in the RAIRS experiments. Compared to acrolein and propanal, the two alcohols, 2-propenol and 1-propanol, have notably higher desorption temperatures and display strong hydrogen bonding in the multilayers as revealed by a broadened and redshifted O-H stretch. For acrolein, the out-of-plane bending modes are more intense than the C=O stretch at submonolayer coverage, indicating that the molecular plane is mainly parallel to the surface. In contrast, the opposite intensity trend was observed for multilayer acrolein, suggesting that the C=O bonds are tilted away from the surface. For 1-propanol, annealing the surface to 180 K disrupts the hydrogen bonding to produce unusually narrow peaks. This indicates that 1-propanol forms a highly ordered monolayer and adsorbs as a single conformer at low coverage. For 2-propenol, hydrogen bonding in the multilayer correlates with the observation of the C=C stretch at 1647 cm^{-1}, which is invisible for the monolayer. This suggests that the C=C bond is parallel to the surface for monolayer coverages of 2-propenol. Similarly, for propanal, the C=O stretch peak at 1735 cm^{-1} compared to those at 1671 and 1695 cm^{-1} is very weak for the low coverage. Still, it becomes the most prominent peak for the multilayer, indicating a change in molecular orientation. These results provided further insights into previous studies [1,2] on hydrogenation pathways of acrolein on the Ag(111) and Pd-Ag(111) SAA surface and into the challenges of selectively increasing the yield of the unsaturated alcohol.

References:

[1] Muir, M., et al., J Phys. Chem. C (2020) 124 (44), 24271

[2] Muir, M., et al., Phys. Chem. Chem. Phys. (2020) 22 (43), 25011

HC-ThP-10 Characterizing the Ag/Al_2O_3 Catalyst and Nonthermal Plasma Couple via Native OES Diagnostics, ***Ryan Chapman**, J. Blechle,* Wilkes University

The persistently growing global demand for energy, transportation, and production will inevitably further environmental deterioration by means of hazardous emissions. Minimizing environmental damage thus requires the development of technologies that can mitigate the pollution associated with such anthropogenic sources. The selective catalytic reduction (SCR) of nitrogen oxides (NO_x) is one of the major breakthrough technologies in the abatement of pollutants from vehicular and industrial emissions, and Ag/Al_2O_3 has been widely studied as an ideal catalyst for SCR systems due to its selectivity and tolerance to poisoning by SO_2 and water vapor. However, SCR using Ag/Al_2O_3 exhibits poor efficacy at temperatures below ~250 °C due to diminished activity of the reductant species. A promising means of overcoming these deficiencies is in the synergy between nonthermal plasma (NTP) and Ag/Al_2O_3 catalysts. Despite the potential of plasma-assisted SCR for pollution abatement as shown in the literature, the chemistry underlying the NTP/catalyst couple must be resolved to optimize the process for commercial use.

In order to further explore these synergies, optical emission spectroscopy (OES) is used to characterize a NTP (N_2/O_2/Ar) and Ag/Al_2O_3 couple on the basis of energy partitioning, densities, and formation/decay kinetics of relevant excited states in the plasma bulk. An inverse proportionality between NO^* density and vibrational temperature (T_v) is observed for NTP coupled with Al_2O_3 surfaces (0-10 wt% loadings in Ag). At high input powers (175-200 W), NO^* T_v's increase only marginally in the presence of 2, 5, and 10 wt% loadings, whereas a marked increase is observed in the presence of 0 wt% Ag/Al_2O_3. Even so, NO^* densities are comparably diminished (relative to the density observed at 25 W) for all systems studied. The catalytic role of Ag species in abating NO^* is further explored by the decay kinetics of NO^*. While the initial NO^* emission intensity decays with time for all NTP's coupled with substrate, the decay rate constants were greatest for bulk NTP coupled with 5 and 10 wt% Ag/Al_2O_3. Differing formation and decay behaviors of the excited states are observed with successive plasma treatments, depending on the degree of silver loading. Further investigations, such as plasma pre-treatment of the catalytic surfaces and varying surface analyses provide additional insights into the interconnected plasma-surface system. The combination of these data provide a unique insight into the mechanistic behavior and the role of the system conditions on plasma-enhanced SCR.

HC-ThP-11 Analysis of Microsilicon and Nanosilicon for Lithium-Ion Battery Anodes, ***Aaron Hsi**, A. Sheth, C. Chu, A. Suen, S. Annamalai, S. Adibnia, M. Uddin, N. Sangeneni,* Aspiring Scholars Directed Research Program

The abundance and low cost of silicon presents the ideal candidate of silicon anodes as an energy-dense, sustainable alternative to graphite anodes in lithium-ion batteries with a reported theoretical capacity of 4200 mAh/g. However, challenges such as significant volume expansion, rapid pulverization, relatively poor conductivity, and unstable sei layers formed with the use of silicon anodes hinders the practical applications. Micro silicon and nanosilicon demonstrate promise tackling these challenges while utilizing the unique characteristic of silicon due to a larger surface area allowing for greater charge intercalation with the anode material and electrolyte without causing significant volume expansion. We have characterized micro- and nano-silicon with particle size ranges of 50 µm, 20-30 nm, and 150-200 nm through Fourier-Transform Infrared Spectroscopy (FTIR) to evaluate the presence of impurities in our samples and X-Ray Diffraction Spectroscopy (XRD) to determine the crystal structure of our samples. For electrochemical characterization, we utilized cyclic voltammetry (CV) to computationally identify the theoretical capacitance of different micro and nano-silicon-based inks (combinations of carbon black and silicon) deposited on nickel foam electrode material. Likewise we utilized Galvanostatic Charge Discharge (GCD) to identify performance characteristics of the material in battery type conditions identifying energy density, power density, and Coulombic efficiency. Our FTIR analysis indicated nano-silicon of particle sizes ranging from 20-30 nm was more prone to oxygen-related impurity formation due to a strong peak at 1071 cm-1 that corresponds to the asymmetric vibration of Si-O bonds. Through our computational analysis, we found theoretical specific capacitance values of 23.59 F g-1.of nanosilicon 01 (150-200 nm), 22.04 F g-1 of nanosilicon 02 (20-30 nm) , and 23.3 F g-1 of Microsilicon. Through testing optimal parameters of various silicon particle sizes we seek to identify the most efficient size of nano-silicon and evaluate its efficiency in an actual model lithium-ion battery utilizing COMSOL software models.

HC-ThP-12 Chemical Speciation and Structural Evolution of Rhodium and Silver Surfaces with High Oxygen Coverages, ***Dan Killelea**, E. Jamka, M. Gillum, M. Turano,* Loyola University Chicago*; L. Juurlink,* Leiden University, Netherlands

The interaction of oxygen with the surfaces of catalytically active transition metals has attracted much interest because of the relevance to heterogeneous catalysis. Recently, we have shown that oxygen coverages in excess of 1 ML are achievable using gas-phase atomic oxygen (AO) to dose the metal surfaces. This talk will discuss some recent results comparing the uptake of AO and O2 on Ag(111) to Rh(111). On Rh(111), subsurface oxygen readily forms from exposure to AO and the surface phases are dependent on the exposure temperature. We also discovered that subsurface O emerges at defects and alongside surface phase transitions. Finally, the uptake of oxygen on Ag(111) is discussed; unlike Rh(111), where little surface reconstruction occurs, Ag(111) undergoes several phase transformations as the oxygen coverage is increased. These results using AO demonstrate that UHV compatible dosing can prepare the same surfaces resulting high pressure O2 exposures, allowing for quantitative and structural analysis of the oxidized surfaces.

HC-ThP-13 Density Functional Theory Computed Descriptors for Heterogeneous Catalysis of CO_2 Sorbent Amines, ***Joshua Gabriel,*** Argonne National Laboratory, USA

Integrating carbon capture and conversion is a promising direction towards a decarbonized future for industries that are heavily dependent on carbon-based raw materials. Progress has been made in achieving the electrocatalytic reduction of carbon dioxide to carbon monoxide from CO_2 captured in a monoethanolamine solution on silver catalysts. In this work, we use density functional theory calculations to test a hypothesis that the coverage of alkali cation controls the relative binding strength of proposed species of reactants, byproducts, and products, and hence the reaction product selectivity. Our results support the hypothesis that the alkali cation affects the relative binding strength of species for CO_2 reduction and hydrogen evolution, with increased coverage favoring CO_2 reduction. This discovery provides a useful computational descriptor to better understand the process conditions that can control product selectivity in heterogeneous catalysis.

HC-ThP-14 Reactivity of Primary and Secondary Butanol Isomers on TiO_2/Au(111)*, **Haley Frankovich**, L. Garber, A. Galgano, C. Grant, E. Schell, J. Yoo, C. Rogers, J. Carmany, A. Baber,* James Madison University

Biofuels can be used to reduce global dependence on fossil fuels while contributing to a carbon neutral cycle. Biobutanol has low volatility and multiple transportation options which make it an attractive alternative fuel. Understanding the fundamental thermal catalysis processes of butanol over heterogeneous model catalysts can aid in the design of more efficient catalysts. Butanol isomers give rise to products including isobutyraldehyde, 2-butanone, butyraldehyde, isobutene, and butene, all of which have applications ranging from gasoline additives to bioplastics. For the partial oxidation of butanol isomers, TiO_2/Au(111) inverse model catalysts are promising due to their ability to catalyze redox reactions of $C_1 – C_3$ alcohols. Titania coverage effects were not reported for methanol or 2-propanol, but lower TiO_2 coverages in the presence of excess oxygen enhance selectivity of the partial oxidation of ethanol. To better understand how butanol breaks down in heterogeneous catalytic processes, temperature programmed desorption (TPD) is used to investigate its reaction. In this study, the reactivity of butanol isomers, specifically 1-butanol, 2-butanol, and isobutanol, on TiO_2/Au(111) was investigated. TPD was used to detect products and atomic force microscopy (AFM) highlighted the morphology of the surface. At low coverages of TiO_2, only 2-butanol showed expected oxidation reactivity, while, 1-BuOH exhibited low reactivity and formed reduced products, and isobutanol produced the recombinative product. At higher coverages of TiO_2/Au(111), 2-butanol formed both oxidized and reduced products, 1-butanol only formed reduced products, isobutanol produced oxidation, reduced, and recombinative products. The selectivity of the reaction was not altered during successive desorption experiments, indicating that the model catalyst was stable without reoxidation between experiments. AFM images show that the Au(111) crystal has ~0.13 ML and 0.27 ML of TiO_2 with predominantly 1D wire-like nanoparticles. Higher coverages of TiO_2 result in more particles distributed across the surface indicating that the reactivity was influenced by butanol proximity to TiO_2 nanoparticle rather than differences in size or shape.

HC-ThP-16 Synthesis and Characterization of Mixed-Ligand Monolayers on Silver Nanoparticles*, X. Wang, **William Hemmingson**, D. Green,* University of Virginia, USA

Functionalized silver nanoparticles (AgNPs) are high-value materials that have a wide variety of uses including drug delivery and catalysis. To achieve these functions, a self-assembled monolayer (SAM) of ligands is synthesized on the surface of the particle. For a mixture of ligands, it is essential to study how the ligands arrange on the surface since that can affect the properties of the system. In this study, thiolated ligands with varying chain lengths and headgroups consisting of a carboxylic acid or methyl group were synthesized and subsequently characterized using matrix-assisted laser desorption/ionization mass spectroscopy (MALDI-MS). Based on the known fragmentation pattern of AgNPs, the nearest neighbor distribution of the ligands can be determined. However, it was discovered that the fragmentation of AgNPs with carboxylic acid ligands is inconsistent at pH 7. Thus, a sodium salt solution should be added to the sample to promote cationization, which facilitates detection in MALDI-MS. Further, basic (pH=9) or acidic (pH=1) solutions have a higher yield of charged fragments than a pH-neutral sample. However, there is evidence that, under either of these conditions, the fragmentation pattern changes, and that change must be accounted for during analysis. Ultimately, this ongoing study will aid in understanding the functioning mechanisms of high-value AgNPs.

HC-ThP-17 Morphological Studies of TiO_2 Nanoparticles on Au(111)*, **Erin Schell**, J. Yoo, A. Baber,* James Madison University

TiO_2 nanoparticles (NPs) supported on Au(111) form an inverse model catalyst that is active for alcohol oxidation and reduction. To fully understand the influence that the nanoparticle size and structure have on alcohol reactivity, TiO_2/Au(111) catalysts were synthesized and characterized. TiO_2NPs were deposited on Au(111) in an O_2 background under ultrahigh vacuum (UHV) conditions. The reactivity of the TiO_2/Au(111) was tested using butanol temperature programmed reaction spectroscopy (TPRS). Two TiO_2 deposition times were studied, resulting in TiO_2 coverages of 0.13 ML and 0.27 ML, as determined by atomic force microscopy (AFM). In addition to quantifying TiO_2 coverages, the morphology and distribution of TiO_2 NPs were observed with AFM. To obtain the clearest images possible, the TiO_2/Au(111) samples were briefly annealed with a H_2 flame to clean contaminates from the surface. While a brief H_2 flame anneal does not affect the TiO_2morphology, longer flame anneals cause large changes in the morphology consistent with the formation of a mixed metal oxide. With longer TiO_2 deposition time, the TiO_2 coverage increased, but particle size remained the same. Interestingly, the higher coverage of TiO_2 resulted in more consistent reactivity with butanol isomers, whereas the smaller coverage of TiO_2 NPs showed low reactivity. AFM images suggest that the difference in reactivity is likely due to the lower number of particles rather than to differences in the size and shape of TiO_2NPs. These results help to inform the design of more active catalysts for alcohol partial oxidation.

Quantum Information Science Focus Topic
Room Ballroom A - Session QS-ThP
Quantum Information Science Poster Session

QS-ThP-2 Creating, Controlling, and Characterizing Quantum Emission in Hexagonal Boron Nitride*, **Annemarie Exarhos**,* Lafayette College*; D. Hopper, R. Patel, R. Grote,* University of Pennsylvania*; A. Alkauskas,* Center for Physical Sciences and Technology, Lithuania*; M. Doherty,* Australian National University, Australia*; L. Bassett,* University of Pennsylvania

Optically addressable spins associated with localized defects in wide-bandgap semiconductors are the basis for rapidly expanding quantum technologies in nanoscale sensing and quantum information processing. Most research has focused on three-dimensional host materials such as diamond and silicon carbide, but more recent reports of single-photon emission – also known as quantum emission - from van der Waals materials has led to an increasingly active area of research focused on these systems. Within the family of two-dimensional materials, hexagonal boron nitride (hBN) has emerged as a robust host for bright, stable, room-temperature quantum emitters. However, many questions persist regarding the chemical and electronic structure of the defects responsible for emission as well as the potential role of spin-related effects. Significantly complicating the identification is the heterogeneity of optical characteristics observed for these quantum emitters.

Our studies focus on identifying and characterizing the optical and magnetic properties of quantum emitters in suspended hBN films in ambient conditions, via confocal fluorescence microscopy. Some qualitative similarities in optical dipole orientation, spectral shape, and emission statistics are evident among quantum emitters in hBN, even for large variations in emission energy, though some emitters exhibit significantly different behavior, suggesting that quantum emission in hBN may result from chemically different types of defects, different charge states of the same defect, or as the result of strong local perturbations [1]. Significantly, a small percentage of observed quantum emitters exhibit strongly anisotropic photoluminescence modulation in response to an applied magnetic field at room temperature [2]. The magnetic-field-induced modulation is consistent with an electronic model featuring a spin-dependent inter-system crossing between triplet and singlet manifolds, suggesting that these defects host optically addressable spin states. This discovery represents a critical step towards the realization of spin-based quantum technologies using van der Waals heterostructures. More broadly, the experimental considerations and techniques involved in this work provide a roadmap for the future experimental identification of quantum emitters in other wide-bandgap structures, paving the way for the discovery of quantum emitters with varying properties in a variety of hosts for use in future quantum technologies.

[1] Exarhos et al., ACS Nano 11, 3328 (2017).

[2] Exarhos et al., Nature Communications 10, 222 (2019).

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Advanced Surface Engineering Division
Room Ballroom A - Session SE-ThP

Advanced Surface Engineering Poster Session

SE-ThP-1 Can a Nanoindenter be Used as a Hardness Spectrometer?, ***Esteban Broitman***, SKF B.V. - Research & Technology Development, Netherlands

The precise knowledge of material microstructures is of vital importance to understand their mechanical and tribological performance. Standard microstructural characterization, carried out by optical and electron microscopy together with X-ray diffraction, is usually correlated to the hardness determined by Rockwell or Vickers indentation at macro- and microscale, and nanoindentation at nanoscale.

In the first part of the presentation, the background of a novel statistical nanoindentation technique to measure hardness and Young's modulus of materials is described [1]. We indicate how experiments are designed, and how the distribution of the hardness and modulus of elasticity determined from the nanoindentation observations are deconvoluted to generate hardness histograms that reflect unique characteristics (fingerprints) of each coating or bulk material. We show how the statistical deconvolution analyses gives an estimate of the microstructural constituents, their volume fraction and corresponding plastic and elastic properties at nanoscale. In the second part, numerous examples on different kind of coatings and bulk materials are presented to illustrate the usefulness of the novel technique.

We demonstrate that, by using nanoindentation as a novel tool for static nanomechanical spectrometric analysis of coatings and bulk materials, a fundamental understanding of the relation between local microstructure (phases and their size) and local material response during elastic and plastic deformation can be obtained.

[1] *"Microstructural Analysis of Bearing Steels by a Statistical Nanoindentation Technique,"* E. Broitman, M. Y. Sherif, B. Minov, U. Sachadel, Bearing World Journal 5 (2020) 47-54.

SE-ThP-2 Diagnosing Stress in Thin Films with High-Throughput Experimentation and Simulation-Based Methods, ***Matias Kalaswad***, *A. Shrivastava, S. Desai, J. Custer, S. Addamane, M. Rodriguez, P. Kotula, M. D'Elia, H. Najm, R. Dingreville, B. Boyce, D. Adams,* Sandia National Laboratories

Stress in metal thin films is a critical aspect of fabrication processes, as excess residual stress can have a detrimental effect on the reliability, performance, and durability of devices. Although there are well-established methods to determine the amount of residual stresses in thin films, unraveling all sources of stress remains challenging due to the numerous factors involved in thin film deposition. Similarly, efforts to quantify relationships between film microstructure and stress remain challenging because of the multimodal nature of microstructural data. Here we seek to identify material "fingerprints" utilizing high-throughput characterization together with simulations to identify process-structure-property correlations related to the development of stress in metal thin films. Mo thin films were deposited onto oxidized Si wafers by magnetron sputtering over various Ar pressures and sputter powers. Traditional wafer curvature measurements were first performed to obtain average residual stress results consistent with those reported in the literature. An automated, high-throughput XRD process was then used to determine out-of-plane lattice spacings in agreement with the in-plane stress according to the Poisson effect. In-plane images of the film were collected through scanning electron microscopy (SEM) and atomic force microscopy (AFM) complemented by measurements of film resistivity. To supplement the experimental results and add to the multi-fidelity of information, simulations of metal transport were completed to estimate the deposition profile and rate as well as properties of the metallic flux during sputtering.The Monte Carlo code SIMTRA, simulating the transport of atoms from the source to the substrate during PVD, provides estimates of ion energy distributions and angular distributions of arriving species, and these characteristics were then applied to a phase-field model to produce the growth dynamics of microstructures resembling those acquired experimentally (verified by transmission electron microscopy). The synthetic and experimental information was ingested by machine learning models with architectures adept at identifying patterns in multimodal data streams. Initial attempts are made to identify meaningful process-structure-property relationships from the experimental and simulated data using a multimodal-based deep learning model. The deep learning model will be further analyzed to explore the dominant mechanisms that underlie the stress developed in metal thin films.

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SE-ThP-3 Significant Texture and Wear Resistance Improvement of TiN Coatings Using Pulsed DC Magnetron Sputtering, ***Nicholas Richter***, *B. Yang, J. Barnard, T. Niu,* Purdue University; *Y. Zhang,* Los Alamos National Laboratory; *D. Shaw,* Advanced Energy Industries, Inc.; *H. Wang, X. Zhang,* Purdue University

Titanium nitride (TiN) coatings fabricated through reactive sputtering feature a suite of parameters capable of altering the microstructure and properties. Here, we explore the influence of using a bipolar pulsed direct current (DC) power supply in place of conventional DC when depositing TiN coatings, focusing on the influence of pulse frequency. The implementation of a pulsed DC voltage profile promotes a drastic texture change from randomly oriented to strongly TiN(111) across the full range of pulse frequencies. Additionally, higher pulse frequencies promote significant grain size reduction, which directly influences the resulting mechanical properties. Nanoindentation and nanoscratch testing were conducted and revealed a corresponding increase in hardness and wear resistance, respectively. The mechanism for this microstructural and texture change is also explored.

SE-ThP-4 Investigation of Laser Ablation Coating Removal (LACR) for Steel Surface Cleaning and Coating Adhesion, ***William Moffat***, University of Virginia; *J. Provines, S. Sharp,* Virginia Transportation Research Council (VTRC); *S. Agnew, J. Fitz-Gerald,* University of Virginia

Laser cleaning has recently received much attention for its ability to clean and prepare metallic surfaces for recoating and bonding operations such as welding, mold cleaning, surface texturing, paint removal, and for adhesive bonding. Laser ablation coating removal (LACR) is gaining acknowledgment as a potential replacement for the current method of grit blasting for surface cleaning and preparation in niche applications. In this work, the feasibility of using LACR to remove old coatings and corrosion products from carbon steel substrates to prepare surfaces for recoating is investigated. Carbon steel is common structural material used in infrastructure due to its reliable mechanical properties and low cost, but due to its tendency to corrode easily, it must be heavily coated and frequently inspected. Because of the harsh service conditions that low carbon steel components are often exposed to, coatings deteriorate and require removal followed by stringent surface preparation for recoating. Surface preparation is a key step in order to ensure that the newly reapplied coating will adhere and perform as expected over the entire service time of the coatings and meet industry standards. In order to test the effectiveness of laser cleaning for surface preparation, extensive adhesion testing of laser cleaned surfaces is needed to determine the feasibility of laser cleaning for steel surface preparation. To investigate the use of LACR to prepare surfaces, steel plates were subjected to laser ablation coating removal (LACR), induction coating removal (ICR), a combination of ICR and LACR, in addition to the incumbent cleaning method of grit blasting. The surfaces were then recoated using a typical three-layer coating system consisting of both organic (epoxy) and inorganic (silica based) zinc rich primers. Pull-off adhesion testing in addition to detailed surface analysis using scanning electron microscopy (SEM) and profilometry show that despite a lower average roughness on the LACR surfaces (avg. Ra 4 µm), the adhesion is equivalent to that of the grit blasted steel (avg. Ra 12.3 µm). In addition, complementary chemical analysis was performed using both energy dispersive spectroscopy (EDS) and x-ray photoelectron spectroscopy (XPS) on the cleaned surfaces. These results show that LACR is a valid candidate that rivals the incumbent method of grit blasting in terms of safety, cleanliness, and environmental sustainability, for both surface cleaning and preparation.

SE-ThP-5 Study of the Corrosion Resistance and Adhesion of DLC with a CrC/CrCN/Cr Bonding Multilayer Deposited by HIPIMS on AISI 4317 Steel, ***Martin Flores***, *L. Flores,* Universidad de Guadalajara, Mexico; *J. Aguilar, A. Gonzalez,* Universidad Autonoma de Tamaulipas, Mexico

Diamond-like carbon (DLC) coatings are utilized in a wide range of applications to reduce the sliding friction, wear and corrosion resistance of components. AISI 4317 steel is used in machinery bearings for the transport of minerals with sulfur content in port facilities. These bearings suffer from wear and corrosion promoted by sulfide and chloride ions. On many substrates, DLC has limited adhesion, so it is necessary to develop interfaces and bonding layers to overcome this limitation. One way to increase adhesion and reduce corrosion is by metal ion etching using the

HIPIMS technique and gradual bond layers.The metal ion etching was performed with a delay in the synchronized polarization pulse of the substrate with respect to the applied to the Cr target. This work reports the results of the potentiodynamic polarization and Daimler-Benz Rockwell C test methods used to evaluate corrosion and adhesion respectively. Synthetic seawater and seawater plus dilute sulfuric acid were used as electrolytes. Raman spectroscopy was used to study the sp2 and sp3 content of the DLC layer. SEM was used to observe the cross section and corroded surface of coated and uncoated samples of AISI 4317 steel. The structure of the bonding multilayer was studied by XRD. The results show an improvement in the corrosion resistance of the samples coated with the multilayer, the correlation between the adhesion and corrosion tests is analyzed.

Smart Multifunctional Materials for Nanomedicine Focus Topic

Room Ballroom A - Session SM-ThP

Smart Multifunctional Materials for Nanomedicine and Theranostics Poster Session

SM-ThP-1 Electrospun Alligned and Randomly Oriented Fibers Using a Novel Collector*, **Tessa Gilmore**, P. Gouma,* The Ohio State University

Electrospinning is a specialized processing technique for the formation of sub-micron diameter fibers of certain materials including polymers. Electrospinning may be used in the medical field, as in cases of drug delivery or tissue engineering. The orientation of the fibers, aligned or random, can affect the application of the non-woven mat due to the difference in properties. For example, aligned fibers have a higher tensile strength and modulus than randomly oriented fibers. Aligned fibers are also better suited for tissue engineering as they have improved cell proliferation and regeneration. Conversely, randomly oriented fibers are better suited for filtration applications as they can maximize separation of unwanted particulates. In this study, a novel collector and experimental setup were used to create both aligned and randomly oriented fibers during the same experiment. A solution of 15 wt% Polyvinylpyrrolidone (PVP) in ethanol was spun, and a hollow casing of fibers that surrounded the top and sides of the collector was observed. Scanning electron microscopic (SEM) images revealed that the casing had uniaxial fibers along the sides and randomly oriented fibers on the top. Additional experiments are being conducted using Cellulose Acetate (CA), which is a popularly used bioplastic. Cellulose Acetate also is known for being difficult to electrospin due to its tendency to crystalize at the extruder tip. However, this novel setup may mitigate this problem.

SM-ThP-2 Effect of Metal-Mediated Oxidative Stress on Lysosomal Damage/Dysfunction*, V. Sanfilippo, C. Bonaccorso, L. Cucci,* University of Catania, Italy*; R. Inturri,* Fidia Farmaceutici S.p.A., R&D Unità locale Fidia Research sud, Italy*; P. Amico,* Fidia Farmaceutici S.p.A., R&D Unità locale Fidia Research sud , Italy*; S. Vaccaro,* Fidia Farmaceutici S.p.A., R&D Unità locale Fidia Research sud, Italy*; **Cristina Satriano**,* University of Catania, Italy

Lysosomes are specialized vesicles within cells that digest large molecules by hydrolytic enzymes; several studies demonstrated that metallic nanoparticles are degraded in the lysosomes with ionic release in the cytosol that induces cell damage. In this work, we reported the synthesis and characterization of plasmonic nanoparticles for subcellular targeting and intracellular imaging of lysosomes. A fluorescent and colorimetric probe (LysoBC1) was designed and synthesized for the dynamic tracking of Cu^{2+} in living cells, to image lysosomal damage. The cytotoxicity and cellular uptake of metallic nanoparticles of silver and gold nanospheres (AgNS, AuNS), both bare and capped with hyaluronan, were scrutinized either on healthy (mouse fibroblast L929 line) or cancerous (human prostate cancer PC3 line) cells. The nanoparticle chemical structure and surface functionalization resulted critical to control the release of toxic species, i.e., Ag^{+} ions, and the ROS generation process, which inhibits the antioxidant defense system causing mechanical damage to the cell membrane. The nanoparticles were prepared by chemical reduction methods and characterized by UV-visible spectroscopy and dynamic light scattering analyses, to study the plasmonic properties and the hydrodynamic size, respectively. The toxicity of intracellularly ions, the cellular internalization of the systems and the involvement of lysosomes in the cellular stress induced by the treatment was investigated in terms of cell viability, ROS production, and live cell-confocal imaging.

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Keywords: metallic nanoparticles, hyaluronic acid, ROS production, cell confocal imaging

SM-ThP-3 The Interaction of Neurotrophin-Mimicking Peptides and Artificial Cell Membranes: An Experimental and Theoretical Study*, **Vanessa Sanfilippo**, L. Redigolo,* University of Catania, Department of Chemical Sciences, Italy*; G. Forte,* University of Catania, Department of Drug and Health Sciences, Italy*; C. Satriano,* University of Catania, Department of Chemical Sciences, Italy

In the present work we assembled hybrid peptide-nanomaterial (p-NM) systems to scrutinize their interaction at the biointerface with artificial cell membranes in 3D or in 2D, i.e., with phospholipid small unilamellar vesicles (SUVs) or supported lipid bilayers (SLBs), respectively.The peptide sequences BDNF(1-12), NT3(1-13) and NGF(1-14), encompassing the N-terminal domains respectively of Brain Derived Neurotrophic Factor (BDNF), NeuroTrophin 3 (NT3) and Nerve Growth Factor (NGF), were immobilized by physisorption onto graphene oxide (GO). The optical characterization through UV-Vis and Fluorescence spectroscopies, in terms of FRET (Forster Resonance Energy Transfer) has been made to shed light on the electron transfer processes occurring firstly at the interface between carboxyfluorescein-labelled peptides and GO (quencher of fluorescence) and then between the peptide-functionalized GO sheets (FRET donor) and the lipid membranes dye-labelled with rhodamine (FRET acceptor). The biophysical properties of the artificial cell membrane, before and after the interaction with p-NM systems, were investigated by atomic force microscopy (AFM), in terms of morphology, and by laser scanning confocal microscopy (LSM). In particular, the latter was utilized with the Fluorescence Recovery After Photobleaching (FRAP) technique, to study the average molecular lateral diffusion at the hybrid nanobiointerface. 3D optical characterization has been made through UV-Vis and Fluorescence spectroscopies, also in terms of FRET (Forster Resonance Energy Transfer) to understand the electron transfer processes. The experimental studies were paralleled by computational analyses by molecular dynamics. Cellular experiments were carried out to investigate the interaction with HUVECs cells in terms of cytotoxicity, through MTT assay, and cellular internalization, through LSM, after being treated with the p-NM. Moreover, wound closure experiments and tube formation assays were carried out to investigate the cell-migration effects and the angiogenic response induced by p-NM systems.

SM-ThP-4 CTAB Removal and Graphene Oxide Functionalization of Metallic Nanorods for Theranostic Applications*, **Alice Foti**, V. Sanfilippo, P. Tomasella,* University of Catania, Italy*; L. Le Meur, T. Bretot,* University of Rennes, France*; C. Satriano,* University of Catania, Italy

Cetyltrimethylammonium bromide (CTAB) is a strong surfactant which plays a fundamental role in several procedures, such the seed-mediated growth of plasmonic nanorods.

In this respect, CTAB is used as growth and stabilizing agent as it forms bilayers on the surface of the nanorods. However, the dissociation of CTAB into CTA^{+} and Br^{-} makes it toxic for cells, therefore the application of nanorods in biomedical fields has some limitations. Herein, we present a strategy to remove CTAB from the metallic nanoparticle surface, followed by the replacement of the ligand with graphene oxide (GO) and reduced-thiolated GO (rGOSH), to obtain nanoparticles with a low or null level of toxicity, thus suitable for theranostic applications.

Plasmonic properties of the different systems were studied by UV-visible spectroscopy and monitored during time. The surface free energy of the CTAB-capped and CTAB-rinsed nanorods were determined by contact angle (CA) measurements and the surface charge was monitored by zeta potential (ZP) measurements. Atomic force microscopy (AFM) and dynamic light scattering (DLS) measurements were performed to investigate for size distributions and hydrodynamic size of the nanoparticles, respectively. The cytotoxicity was studied *in vitro* on different cell lines by means of cell viability detection by nuclear staining of dead/total cells and mitochondrial enzymatic activity (MTT assay). The reactive oxygen species (ROS) production was determined by MitoSOX assay, laser scanning confocal microscopy (LSM) allowed to shed light on the intracellular organelle perturbation.

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SM-ThP-5 Hydropolymers, Hydrogels and Hydrogel Composites as Lubricants*, **Nir Kampf**, W. Lin, M. Kluzek,* Weizmann Institute of Science, Israel*; S. Angayarkanni,* SRMIST, India*; N. Iuster, E. Shimoni,* Weizmann Institute of Science, Israel*; R. Goldberg,* lipo-sphere, Israel*; J. Klein,* Weizmann Institute of Science, Israel

About 20% of the world's total energy consumption spent to overcome friction. Friction is also present water-based environments like biological systems, widely in hips and joints.Due to the molecular complexity of the biological systems, the mechanism of lubrication is still not clear. Apart from our efforts to find the major components responsible for the low friction in biological systems, we also try to exploit nature's solution for lubricating interfaces such as cartilage by mimicking nature's strategies of boundary lubrication, which lead to an extreme reduction of friction in aqueous environments. Low frictions failure in joints is correlated with diseases such as osteoarthritis. In my talk, I will present several examples of bio-inspired lubrication by polymers and in polymer networks. We carried out systematic investigations from the molecular to the macroscopic level, demonstrating excellent lubrication by polymer assemblies (1) and hydrogel composites (2), attributed to the hydration lubrication mechanism acting at highly-hydrated boundary layers.

1) Angayarkanni et al., (2019) Langmuir. 35, 48, p. 15469-15480.

2) Lin et al., (2020) Science. 370, 6514, p. 335-338.

SM-ThP-6 Nanocomposites of Gold Nanoparticles-Graphene Oxide and Angiogenin for Wound Care Treatment*, L. Chiaverini, T. Marzo, **Diego La Mendola**,* University of Pisa, Italy

Hybrid platforms made of gold nanoparticles (AuNPs), graphene oxide (GO) nanosheets and angiogenin (ANG) protein were prepared to tune angiogenic process in the wound healing treatment.

Nanocomposites were characterized by UV-visible spectroscopy, to scrutinise the ANG binding to Au-GO, by monitoring the changes in the plasmonic peak (AuNP) as well as in the π->π* transition electronic band (GO), respectively. Atomic force microscopy and dynamic light scattering analyses confirmed a strong association of the protein to nanoparticles/nanosheets. Cellular experiments on human foreskin fibroblasts demonstrated the low cytotoxicity of the nanocomposites and theiractivity in promoting wound closure. Cell imaging by confocal microscopy revealed synergic dynamic processes modulated by the different sub-cellular structures. The obtained results evidence the promising applications of the synthesized multifunctional nanocomposites for wound care treatment.

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SM-ThP-7 Novel Synthesis of Silver Nanoparticles and Their Antibacterial Activity for Therapeutic Applications*, H. Arshad,* Rutgers, The State University of New Jersey*; **Umer Hassan**,* Rutgers The State University of New Jersey

Silver nanoparticles (AgNPs) finds many biomedical applications due to their antimicrobial activity. Traditional material synthesis process employed to fabricate these nanoparticles require hazardous chemicals thereby posing a significant personnel and environmental risk. To mitigate this, we developed a novel eco-friendly fabrication process to synthesize silver nanoparticles using plant extracts. Here, we report the utility of Salvadora persica extract as reducing agent for nanoparticle synthesis. Further, we employed sunlight and LED irradiation methods for AgNPs fabrication. Nanoparticles were synthesized within 10 min and were characterized using multiple techniques. UV–Vis. absorbance spectroscopy analysis demonstrated spectral peaks at 450 nm corelative to AgNPs synthesis while X-ray diffraction (P-XRD) pattern depicted nanoparticles crystal structure. Fourier transform infrared spectroscopy (FTIR) demonstrated the role of phytochemicals for AgNPs reduction. Morphological analysis was done using transmission electron microscopy (TEM) and field emission scanning electron microscopy (FE-SEM) which demonstrated nanoparticles spherical shapes and revealed their size of approximately 39.7nm.

Synthesized AgNPs were extensively characterized for their antibacterial activity against Escherichia coli (E. coli) and Staphylococcus epidermidis (S. epidermidis) pathogens. Kirby Bauer antimicrobial assay was used for this analysis, and minimum bactericidal concentration (MBC) and minimum inhibitory concentration (MIC) were calculated. For E. coli MBC and MIC were determined to be 3.0 μg/mL and 1.5 μg/mL respectively. However, for S. epidermidis, these values were determined to be 25 μg/mL and 12.5 μg/mL respectively. This study highlights a novel nanoparticles fabrication method and provide their extensive characterization analysis with a focus on their role in antibacterial activity for therapeutic applications. These nanoparticles can be used to design next generation wound dressings or impregnated in surgical masks to provide enhanced antimicrobial protection.

Thin Films Division
Room Ballroom A - Session TF-ThP
Thin Film Poster Session

TF-ThP-1 Effect of Metallic Bonding on the Optical Properties of Transition Metal Based Thin Films*, **Nimarta Kaur Chowdhary**, T. Gougousi,* UMBC

Combining electronics and photonic devices on a single chip provides a powerful approach to resolving technological issues, from solar technology to low-power computing systems. Next-generation high-speed photonic devices require materials with large and fast optical nonlinearities. Integrating electronic and photonic devices on a single chip has proved challenging due to the limited availability of nonlinear materials compatible with the semiconductor industry process flow. Transition metal oxide thin films may serve as a potential solution to this problem.

It has been shown that atomic layer deposition (ALD)-grown as-deposited TiO_2thin films demonstrated large $n_2$values, which were 4-6 orders larger than previously reported [1]. X-ray photoelectron spectroscopy (XPS) revealed that these TiO_2 films incorporated Ti-O-N/TiN metallic bonds during growth [1]. The very large enhancement that occurred for ALD films grown at 250 °C was a result of about 1 at. % of Ti-O-N bonds evenly distributed within the films [1]. Although silicon and most dielectric materials used in the electronic industry show little to no nonlinear optical response, it is predicted that the addition of metallic impurities in the bulk during the fabrication process will be an optimal way to induce nonlinearities while maintaining compatibility with the process cycle.

We investigated two complementary ways to incorporate metallic bonding starting with either metal oxide (hafnium dioxide, titanium dioxide) or metal (titanium, titanium nitride) thin films. The former is grown using ALD, and to enhance the metallic bonding, we attempted to promote precursor decomposition by using growth parameters such as temperature and purge times outside the optimal ALD window. Metal films were grown by physical vapor deposition (PVD) and post-deposition thermal treatment was used to control the amount of metal bonding. The ALD films showed some metallic bonding that was accompanied by an increased concentration of bonded carbon impurities. This metallic bonding was found to affect the films' bandgap with absorption extending further into the visible than for pure TiO_2 films.

This approach to accomplishing large nonlinearities may be transferable to other transition metals/transition metal oxides and their nitrides. This will diversify the toolkit of nonlinear optical materials available in the thin-film form, which in its current state is severely lacking.

[1]R. Kuis, T. Gougousi, et al, *ACS Photonics*, vol. 6, no. 11, pp. 2966–2973, Nov. 2019, doi: 10.1021/acsphotonics.9b01176.

TF-ThP-2 Water Transfer of Electronic Circuits on Flexible and Stretchable 3D Objects*, **Issraa Shahine**,* Nantes Université, CNRS, Institut des Matériaux de Nantes Jean Rouxel (IMN). iété d'Accélération du Transfert de Technologie, SATT Ouest ValorisatSocion SAS, France*; M. Harnois,* Université Rennes 1, CNRS, Institut d'Électronique et des Télécommunications de Rennes (IETR), France*; P. Tessier,* Nantes Université, CNRS, Institut des Matériaux de Nantes Jean Rouxel (IMN), France

There is a growing need for products that integrate active electronic devices on the surface of everyday complex objects to make them smarter and more connected. Often the presence of electronic circuits on the surface must remain relatively discreet. It is then necessary to have transparency of the circuit connections. It is a main concern of the field of 3D electronics for "smart objects" and "smart sensors" as an important part of display devices (touch screen and display), energy storage devices (solar cells and super capacitors), and wearable medical devices (electronic skin).

Herein, we use a new and original process for transferring 3D electronic circuits, to produce the interconnection of the transferred circuits over 3D objects conserving their optical, electronic and mechanical properties, to finally serve as flexible transparent conductive electrodes (FTCE).The aim is to connect SMD (surface mounted device) to the defined design circuits to validate the overall operation of the object at the level of detection, display and communication functions.

For this aim, we fabricate, by physical vapor deposition (PVD) method, flexible, stretchable and transparent nanoporous gold designs resulted by applying dealloying process to ultra-thin Au-Cu alloy thin films using acidic vapors.[1] [#_ftn1] These designs are transferred into defined flat and/or 3D surfaces according to the process of film-based patterns transferred to 3D object surfaces.[2] [#_ftn2] This new, powerful and robust technology allows a good transfer of manufactured lines with correct performances concerning the transmittance and sheet resistance of the transferred thin films to deformation.

The transfer into flexible PET surfaces allows the conservation of the electrical properties of the design upon deformation. They have good sheet resistance values ranging from few to about tens of ohms per square (Ω/□), with a transparency of the order of 50%, while maintaining exceptional stability under severe mechanical deformations (bending).

[1] [#_ftnref1]*Chauvin et al. (2019), NPJ Flexible Electronics, 3(1), 1-6.*

[2] [#_ftnref2]*Le Borgne et al. (2017), ACS applied materials & interfaces, 9(35), 29424-29429.*

TF-ThP-3 Magnetic Field Assisted Epitaxial Growth of Magnetite Films

Adam Dziwoki, Jerzy Haber Institute of Catalysis and Surface Chemistry PAS, Poland*; B. Blizniuk,* Jerzy Haber Institute of Catalysis and Surface Chemistry, PAS, Ukraine*; K. Freindl, J. Korecki, N. Spiridis,* Jerzy Haber Institute of Catalysis and Surface Chemistry, PAS, Poland

Modern spintronics requires materials, usually thin films and heterostructures, with controllable and programmable magnetic properties. One of the key properties is magnetic anisotropy that determines the orientation of magnetization and its response to an external magnetic field (MF). In well-defined epitaxial films the main contributions to the effective magnetic anisotropy are shape, magnetocrystalline, surface/interface and magnetoelastic/strain anisotropy terms. Molecular beam epitaxy (MBE), which is the most widely used method of growing magnetic heterostructures allows certain level of indirect control of the magnetic properties by controlling elementary growth processes through substrate temperature, deposition rate and partial pressure of reactive gases. Additionally, external agents can be used, such as plasma generation or ion beams. Other factors, including external stimuli, have been only occasionally applied in physical vapor deposition of thin films. In particular, due to the limitations of the MBE technology, examples of application of external fields (in particular MF) *in situ* during growth, as well during *in situ* post-deposition treatment are scarce. Here we present MF-assisted epitaxial growth of magnetite Fe_3O_4(001) films on MgO(001) and Fe_3O_4(111) on Mg(111).

The magnetite films were deposited in a multi-chamber ultra-high vacuum (UHV) system (base pressure $5\cdot10^{-10}$ mbar) including MBE facility, typical surface characterization tools (LEED, AES, STM) and Conversion Electron Mossbauer Spectroscopy (CEMS). We used the typical reactive deposition of metallic ^{57}Fe in O_2 (partial pressure $5\cdot10^{-6}$ mbar) [1]. The use of the ^{57}Fe isotope facilitated CEMS measurements. external MF can be applied during deposition by combination of modular sample holders transferable between two stations of a 4-axis manipulator that are specialized for a given step in the MBE process. The MgO substrates were mounted on “flag-style” (FS) sample plates and the corresponding manipulator station enables those preparation steps that do not require MF. MF can applied using PTS-style sample holders (PREVAC) incorporating permanent magnets and receiving the FS plates. The magnetic field configurations during deposition can be 100 mT in-plane and 250 mT out-of-plane for the two holder types at maximum deposition temperature of 400°C.

The role of external MF for the in-plane and out-of-plane magnetic anisotropy in the Fe_3O_4(001) and Fe_3O_4(111) film is revealed by the CEMS analysis that is able to distinguish between different magnetization orientation in the virgin magnetization state.

[1] J. Korecki et al. Thin Solid Films. 412(2002)14.

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TF-ThP-4 Spectra Analyses of Antirreflection Coatings and Hydrogeneted Amorphous Silicon Deposited at Room Temperature for Silicon Photovoltaic Cells Aplications

H. da Silva Alvarez, A. Roberto Silva, F. Hummel Cioldin, L. Carvalho Jayme Espindola, ***José Alexandre Diniz,*** University of Campinas, Brazil

For the application in c-Si PV cells, this work has as its main objective, the analysis of antireflection coatings of thin oxides (TiO_2, Al2O3, Ta_2O_5) and nitride (SiN_x) films, deposited at room temperature, respectively by reactive sputtering or ECR-CVD, for increasing of solar cells efficiency. And of a-Si:H thin films deposited in an ECR-CVD system with RF frequencies of 1W, 3W, and 5W (a-Si:$H_{1W/3W/3W}$), for variations in their hydrogen concentration, after and before the diffusion of aluminum (Al) at the low temperature of 450 °C for future use as emitter layer. Using a UV/VIS/NIR spectrophotometer with an integrating sphere, the total reflectance of these films was calculated by comparing them with the spectra of a polished c-Si control sample (ΔR_{Total}). For the ARC films, ΔR_{Total} higher than 50% were achieved, with the largest ones coming from SiN_x, with 58.6%, and Ta_2O_5, 56.5%. Their respective minimum (R_{min}) were 1.4% and 2.5% at 610 nm and 600 nm – close to the maximum energy in the solar spectrum at 630 nm. The TiO_2 and Al_2O_3 films had corresponding ΔRTotal of 54.6% and 51.7%, with R_{min} of 5.3% and 5.9%, at 580 nm and 530 nm – shifted towards the UV region compared to the ideal value of 630 nm. For the a-Si:H films, it was observed a reduction of the polished c-Si reflection after their deposition, with the best result coming from the a-Si:H_{3W} film with 47.4 %, with R_{min} = 1.4 % at 630 nm. Followed by the sample with the a-Si:H_{5W} film with ΔR_{Total} = 35.1 % and R_{min} = 11.6 % at 670 nm. While, for the a-Si:H_{1W} film, a ΔR_{Total} = 8.2 % was obtained, with R_{min} = 3.0% at 570 nm. This low ΔR_{Total} value of the a-Si:H_{1W} sample is due to the presence of greater reflectance values on its spectra in the regions between 440 nm and 500 nm and 660 nm and 1100 nm when compared with the polished c-Si control sample. After a quickly sputtering deposition (20 s) of an ultrathin Al film and its diffusion for 30 min at 450 °C, Al-$Si_{1W/3W/5W}$ films were produced. After this process, the Al-Si_{5W} has now the best results with ΔR_{Total} = 24.8 %, R_{min} = 20.0 % at 750 nm, and the smallest change in its ΔRTotal. While the Al-Si_{3W} has an intermediate value of ΔRTotal = 8.2%. And the Al-Si_{1W} has a higher reflectance than the polished c-Si substrate with ΔRTotal = -12.6%, negative for this reason. In addition, as the spectra of the films have a similarity with the polished c-Si in the UV region, a change in their crystalline structure could be inferred, probably induced by the Al diffusion.

TF-ThP-5 Characteristics of Low Temperature Deposited SiO_2 Film based on Very High Frequency Plasma Enhanced Atomic Layer Deposition with Substrate Bias

Yongki Lee, *H. Kim, G. Ahn, G. Yeom,* Sungkyunkwan University (SKKU), Republic of Korea

This study investigated the effect of very high frequency (VHF) plasma and substrate biasing on the surface chemical reaction and the surface damage on SiO_2 film deposited at low substrate temperatures by Plasma-enhanced atomic layer deposition (PE-ALD) system. PE-ALD uses plasma to deliver the energy required for chemical reactions and it can be useful in lowering substrate temperature and increasing the density of material during PE-ALD, however, it can also contaminate or damage the substrate by high energy ions in the plasma. In addition, the substrate biasing may also cause unnecessary effects, especially in non-metallic materials such as preferential sputtering of high sputter yield component, charging, etc. In this study, the effect of substrate biasing was optimized while increasing the density of the plasma using VHF plasma. By applying an appropriate bias voltage to the substrate with VHF plasma, it was possible to deposit stoichiometric SiO_2 films with more rigid properties and even at a lower temperature. These results were investigated for both bare and pattern wafers. Therefore, by using optimal combinations of VHF plasma and substrate biasing, improved properties of SiO_2 films deposited at low temperatures in PE-ALD based systems could be realized. SiO_2 has good insulation performance when it is deposited at least 350°C, therefore, if this can be realized at the level of 50°C by using substrate biasing and VHF plasma, it will be helpful to the fabrication of semiconductor devices using new materials. In this presentation, the detailed properties of materials and plasmas deposited by substrate biasing and VHF plasma will be presented.

TF-ThP-6 Sio$_2$ Bottom-Up Trench Fill of a High Aspect Ratio Hole by Plasma Enhanced Atomic Layer Deposition Using a Very High Frequency Plasmas and Inhibitor Surface Treatment*, **Gyuhwan An**, H. Kim, Y. Lee, G. Yeom,* Sungkyunkwan University (SKKU), Republic of Korea

As the semiconductor device size is decreased to nanoscale, even though various trench fill methods such as HARP (High Aspect Ratio Process), HDP (High Density Plasma), and SOG (Spin On Glass), etc. are utilized, the SiO_2 fill process is facing limitations and has become one of the important processes as semiconductor devices become smaller and as the aspect ratio of the trench is increased significantly. In this study, the effects of capacitively coupled plasma-type very high frequency plasmas (VHF) and inhibitor surface treatment during the plasma enhanced atomic layer deposition with DIPAS (Di-isopropylamino Silane]. Formula, H3Si[N{(CH)(CH3)2}] precursor on the SiO2 trench fill characteristics were investigated to improve performance of trench fill, and especially, to obtain the bottom-up type SiO2 fill with low defects such as seam and voids. The deposition film quality was verified through wet etch rate (WER. diluted HF), X-ray photoelectron spectroscopy (XPS), and fourier transform infra-red (FT-IR) analysis, and the analysis was conducted according to the frequency of the plasma source and with different inhibitor conditions. The improvement of fill performance in patterns using inhibitor was analyzed with scanning electron microscopy while changing the trench aspect ratio from 15:1 to 40:1.

TF-ThP-8 Using Metal Precursors to Passivate Surfaces for Area Selective Deposition*, **Kinsey Canova**, L. Souqui, G. Girolami, J. Abelson,* University of Illinois at Urbana-Champaign

We previously showed that co-flowing a non-reacting, gas phase inhibitor during chemical vapor deposition (CVD) greatly enhances the area-selective deposition (ASD) of a metal film on metal instead of on oxide substrates.Here, we employ CVD precursors, which ordinarily react to grow metallic films at temperatures ≤ 300 °C, to inhibit nucleation. This occurs in a temperature window above the onset temperature (T_g) where the intended growth precursor will react to grow film, but below the onset temperature where the second precursor – here acting as an inhibitor – reacts.The latter strongly adsorbs on, and decreases the reactivity of, nucleation sites on the intended non-growth surface.The advantages of using precursors as inhibitors are that: (i) potential “inhibitor” precursors can be identified as those with dense adsorption on the non-growth surface and low reactivity towards the ligands of the intended growth precursor; (ii) they are easily integrated into the CVD process flow; and (iii) they can later be removed from the surface by thermal desorption, pyrolysis, or an atomic layer deposition half-reaction.The precursors we use as inhibitors are $Hf(BH_4)_4$ (T_g = 170 °C) or $Al(CH_3)_3$ (T_g = 300 °C), and these precursors respectively block growth from $AlH_3N(CH_3)_3$ (T_g = 130 °C) or $Hf(BH_4)_4$. Experiments with parallel dosing on metal (growth) and oxide (non-growth) surfaces are used to show the enhanced selectivity from this route. We summarize results by proposing selection criteria for other precursor-inhibitor systems: sort precursors by the T_g, select a precursor for the desired film, then choose an inhibitor that has a higher T_g than, and is unreactive towards, the desired film precursor.For ASD, the inhibitor must densely adsorb and passivate the sites that normally lead to nucleation, e.g., hydroxyl or defect sites on oxide surfaces, and there must be surfaces intended for growth where it adsorbs sparsely or not at all.

TF-ThP-9 Amorphous GeSe Thin Films Prepared by Magnetron Co-Sputtering with Rapid Thermal Annealing for UV Optoelectronic Applications*, S. Pech,* Chosun University, Cambodia*; **Sara Kim**, Y. Jun, N. Kim,* Chosun University, Republic of Korea

GeSe is one of the IV-VI semiconductors with a p-type conductivity and a modest band gap, which gives rise to potential in optoelectronic applications such as photodetectors for communication, imaging, remote sensing, and spectroscopy due to its relative earth-abundance, simple binary composition, and non-toxicity [1,2]. The GeSe was noted as a good photoresponse over a broad range of wavelengths from ultraviolet (UV) to near-infrared with on/off switching properties [3]. In this study, GeSe was deposited by using the radio frequency magnetron co-sputtering systems with Ge and Se targets. The GeSe thin films were annealed as an increase in the annealing temperature from 300 to 500 ℃ by using a rapid thermal annealing system. Compositions and surface characteristics of the GeSe thin films were examined by using an energy dispersive X-ray spectroscopy and a field-emission scanning electron microscope. The surface morphological profile and Crystal structure of the GeSe thin films were analyzed by using an atomic force microscope and X-ray diffraction. Optical properties and Hall characteristics of the GeSe thin films were analyzed by using a UV-Visible spectrometer and Hall effect measurement system. As a result of the analyses, the amorphous nature of the selected thin films was verified in all annealing temperature conditions, and a slight compositional difference occurred; however, a sudden difference in UV transmittance of the GeSe thin films occurred in specific annealing temperature conditions. Acknowledgment: This work was supported by the Gwangju·Jeonnam Local Energy Cluster Manpower Training of the Korea Institute of Energy Technology Evaluation and Planning (KETEP) grant funded by the Korea government Ministry of Trade, Industry and Energy (No. 20214000000560). [1] Amir Muhammad Afzal et al., ACS Appl. Mater. Interfaces 13, 47882 (2021). [2] Ding-Jiang Xue et al., J. Am. Chem. Soc. 139, 958 (2017). [3] Zhenhua Wang et al., ACS Appl. Electron. Mater. 1, 2236 (2019).

TF-ThP-10 Considering XPS Characterisation of Ultra-Thin Films*, J. Counsell, S. Coultas,* Kratos Analytical Inc., UK*; **Christopher Moffitt**,* Kratos Analytical Inc.

Shrinking device dimensions has increased the use of atomic layer deposition (ALD) due to the need for increased control of layer thickness and uniformity. The ability to deposit high dielectric constant (high-k) films via ALD has allowed for their widespread use in a swath of optical, optoelectronic, and electronic devices.

For device design control and optimisation, it is vital to have accurate, quantitative methods to determine thicknesses and structure. We apply and discuss different thickness calculations using both conventional 1486eV and high-energy AgXPS (Ag Lα radiation - 2984eV) to elucidate the structure of ALD thin films of hafnia, alumina and a loayer combination of both.

TF-ThP-11 Characterization of Polycrystalline Hf-doped Ga_2O_3*, **Sara Chamberlin**, V. Singh,* Washington and Jefferson College*; S. King,* University of Wisconsin - La Crosse

Previous work has shown low concentrations of hafnium (Hf) incorporated into Ga_2O_3 single crystals act as a shallow donor, increasing carrier concentrations and lowering the resistivity of the crystal [1,2]. However, only a single concentration of Hf was considered within these studies. To investigate the impact that Hf concentration has on the optical, structural, and morphological properties of the material, polycrystalline films of Hf-doped Ga_2O_3 were deposited at room temperature by reactive RF-sputtering onto silicon and fused silica substrates with varying concentrations of Hf, and were subsequently characterized by spectroscopic ellipsometry, UV-VIS spectrophotometry, x-ray diffraction, x-ray photoelectron spectroscopy, and atomic force microscopy.

Initial results show that all films, regardless of Hf concentration, are initially amorphous, but crystalize as β-Ga_2O_3 upon subsequent annealing, with the possibility of phase segregation when Hf concentrations reach approximately 3 at. %, giving an indication as to the solubility limit of Hf in Ga_2O_3. Spectroscopic ellipsometry measurements show that the index of refraction of the film is altered by Hf incorporation, while UV-Vis measurements show that the optical bandgap is not significantly altered. These results suggest that Hf-doped Ga_2O_3 may find use in optoelectronic devices and applications.

[1] https://iopscience.iop.org/article/10.1088/1361-6641/ab75a6

[2] https://aip.scitation.org/doi/10.1063/5.0062739

TF-ThP-12 A Novel Direct Current Chemical Vapor Deposition (DC-CVD) Reactor for Large Area Diamond Deposition*, G. Major, A. Lizarbe,* Brigham Young University*; B. Lawrence,* Exolv*; **Matthew Linford**,* Brigham Young University

Diamond has diverse applications because of its high hardness, thermal conductivity, chemical inertness, high melting point, and high refractive index. Synthetic diamond is grown in a variety of ways, each having its advantages and disadvantages. For example, high quality, single crystal material can be grown by the high-pressure high-temperature (HPHT) method. However, the size of HPHT diamonds is limited by the size of the anvils used to produce them, and diamond thin films are not possible. Microwave chemical vapor deposition (MWCVD) is widely practiced, where MWCVD reactors are relatively inexpensive. However, MWCVD suffers from both significant plasma inhomogeneities across its growth area, as well as a limited growth area. Here, we describe a novel system based on direct current (DC) CVD, which, when compared to MWCVD, allows for larger growth areas, single-crystal growth, and more uniform growth due to a more consistent temperature and plasma across the growth surface. Our system has a growth diameter of 130 mm, which, in part, leads to a somewhat slower growth rate. However, the larger growth area allows for increased production overall. Diamonds produced in this reactor have been analyzed by Raman spectroscopy, X-ray topography, electron spin resonance, and optically detected magnetic resonance. These analyses showed minimal non-diamond growth, few defects, and uniformly oriented growth among the samples. Future developments include adding dopants, increasing diamond quality, exploring nitrogen vacancies for use in quantum computing, and other novel applications that are made accessible because of the reactor design.

TF-ThP-13 Surface Modification of Additively Manufactured Materials via Stress Gradients on Thin Film Growth*, **Andrew Miceli, S. Stagon,* University of North Florida

Thin surface coatings, ranging from nanometers to microns thick, are commonly used to modify the performance of parts made from injection molding, machining, and 3D printing. These surface coatings, often composed of metal or metal oxide/nitride, are commonly added through physical vapor deposition (PVD). As these coatings are grown in kinetically limited conditions, large residual stresses may form during growth. In this work, we hypothesize that these intrinsic residual stresses may be used advantageously to preferentially modify the stress state experienced by the coated part via preloading effect. First, Finite Element Modeling (FEM) is used in this study to analyze the hypothesis. Using FEM, dog-bone specimens are tested in uniaxial tension using simulated coating surface pre-load stress in both tension and compression. Local stress magnitudes are determined on average by the von-Mises stress throughout the model after simulation is completed. This model is then analyzed to determine average stress of the material and which preload stress state reduces average stress through the material. It was found that in the typical tensile test load case, tensile preloading decreases overall stress of the specimen in the gauge section by up to 12%, thus lessoning chance of failure due to this lower average stress. This FEM study will be complemented by validation experiments where 3D printing will be used to rapidly fabricate polymeric (ABS) and additively manufactured metal (316SS) parts which will be subsequently coated using PVD and tested in tension. Surface characterization of the thin films will be analyzed visually using Scanning Electron Microscopy and Microhardness tests to validate and characterize the alloy composition based on stoichiometric effects. Following surface characterization, Energy Dispersive Spectroscopy will be used to analyze chemical composition of the thin film alloy created. Following uni-axial testing, fully reserved loading will be investigated to study the effects of compressive stress in PVD coatings on fatigue and results will be translated to high-value metal 3D printed parts.

TF-ThP-14 Decoding Thickness Profiles: Conformality as a Tool to Study Process Kinetics*, **Andreas Werbrouck,* Stanford University, Belgium*; V. Cremers, J. Dendooven, C. Detavernier,* Ghent University, Belgium

While the majority of atomic layer deposition (ALD) research is directed towards developing new precursors, reaction chemistries, and applications, fundamental research on ALD conformality is interesting in its own right. Traditionally the focus in ALD conformality research has been on understanding and optimizing the precursor exposure necessary to completely cover complex 3D structures. On the contrary, this work is concerned with incompletely covered structures – more specifically holes. As the deposition proceeds, various parts of the hole receive different exposures: the top of the structure will be exposed to more precursor than the bottom. As a result, the film thickness depth profile in a hole encodes at least the same kinetic information as a traditional saturation curve but spatially resolved instead of temporally.

In order to decode the information hidden in such a thickness depth profile, two existing feature-scale simulation models were reimplemented. The reactive diffusion in the hole can be described with either a system of coupled differential equations [10.1002/cvde.201106938] or a Markov chain simulation [10.1007/s00214-014-1465-x]. Our implementation of these models was validated and subsequently used to fit experimentally obtained profiles.

The power of fitting simulated depth profiles to experimental data was demonstrated by studying plasma-enhanced ALD. With our approach, we were able to determine the partial pressure of reactive oxygen species generated in various reactor conditions (fig. 1).

A second application is in the study of reaction kinetics. As far as we know, current literature only uses first-order Langmuir adsorption to model kinetic interactions between the precursor and the substrate. Still, real-world reaction kinetics may be more complex. By allowing the model to use a general parametrized absorption function instead of a first-order model and fitting this along with the profile, useful kinetic information can be obtained. This is demonstrated with the trimethylaluminum (TMA)-water process, where the TMA step exhibits ideal first-order kinetics, but the reaction of water with the substrate is more complex. It has been suggested previously that this reaction might have a coverage-dependent activation energy [10.1021/acs.jpcc.9b11291 [10.1021/acs.jpcc.9b11291]], and our current results confirm this finding.

TF-ThP-15 Low-Temperature Synthesis of Crystalline VO_X Films via Hollow-Cathode Plasma-Assisted ALD: Impact of Vanadium Precursor*, **Adnan Mohammad, K. Joshi, S. Ilhom, B. Wells,* University of Connecticut*; A. Kemal Okyay,* Stanford University*; B. Willis, N. BIYIKLI,* University of Connecticut

Vanadium oxide exhibits phase-change properties at different stoichiometries including the famous metal-insulator transition (MIT) for VO_2around 70 °C shifting between monoclinic to tetragonal rutile structure phase with temperature change. Such layers have the potential to be used forlow-power electrical switches. The existing VO_x ALD reports demonstrate mainly as-grown amorphous VO_x films via thermal atomic layer deposition (ALD) using TEMAV and VTIP metal precursors and water vapor or ozone as co-reactant. These amorphous films are shown to transform in various crystalline phases using post-deposition annealing process at high temperatures (typically higher than 500 °C). However, no significant report is yet found on low-temperature as-grown VO_2 films grown by thermal or plasma-ALD.

Our main goal in this study is to demonstrate as-grown crystalline VO_x films using our customized hollow-cathode plasma-ALD reactor at substrate temperatures lower than 200 °C and to further improve the crystalline quality and transform the phase structure of the deposited VO_x film into the desired VO_2 stoichiometry. We have grown crystalline VOx thin films at substrate temperatures as low as 200 °C using TEMAV as the vanadium precursor and O_2 plasma as the oxygen co-reactant. The resulting as-grown film was crystalline V_2O_5. The recipe for the plasma-ALD experiments was as the following: 0.250 s of TEMAV pulse with 10 sccm of N_2-carrier flow, 50 sccm Ar-purge for 10 sec, 50 sccm O_2 plasma for 10 s, plasma power 50-300 W, followed by another 10 s of Ar purge. To provide enough TEMAV dose into the reactor chamber, the TEMAV precursor cylinder is heated at 110 °C. The resulting films are crystalline V_2O_5 with a growth per cycle (GPC) value reaching ~2 Å and a refractive index of 2.45. The corresponding growth process has been real-time monitored with *in-situ* ellipsometry depicting the individual chemisorption and ligand exchange surface reactions.

Having accomplished our first goal, our next step is to explore VTIP as the metal precursor: will we obtain similar as-grown crystalline VOx films and if yes, which crystal structure and stoichiometry will dominate? The gain knowledge will be used to further improve and transform the crystal structure of V_2O_5 films. The resulting VO_2 films are characterized for their temperature-dependent electrical properties to validate the MIT behavior, paving the way for prototype electronic switch devices.

TF-ThP-16 Dielectric Property on the Post-Heating Treatment of PVDF Thin Film Prepared by Atmospheric Pressure Plasma Deposition*, **Eun Young Jung,* Kyungpook National University, Republic of Korea*; C. Park,* Milligan University*; H. Tae,* Kyungpook National University, Republic of Korea

Recent developments of piezoelectric nanogenerators (PENGs) for industrial application, will be flexible and stretchable electronic devices with light weight. The piezoelectric polymers seem to be promising alternatives for flexible PENGs. In present, polyvinylidene fluoride (PVDF) has been widely used due to its unique properties such as mechanical flexibility, high chemical resistance, biocompatibility, and high temperature resistance [1,2]. However, this PVDF polymer has still lower piezoelectric characteristics when compared with piezoelectric ceramics. Thus, it is necessary to improve the piezoelectric and dielectric property of the conventional PVDF material for flexible PENGs. Many researches have been mostly investigated on the piezoelectric polymer-nanocomposites with nano-particles in order to develop dielectric materials with high dielectric coefficient for flexible PENGs [1,3]. Accordingly, we examine the effects of the post-heating on the structural and dielectric properties of PVDF thin film deposited by atmospheric pressure plasma (APP) system. The structural and dielectric properties of PVDF thin film were systematically investigated by using field emission-scanning electron spectroscopy (FE-SEM), X-ray diffraction (XRD), Fourier transforms-infrared spectroscopy (FT-IR), LCR meter according to post-heating in order to remove the N,N-dimethylformamide (DMF) element and enhancing the chemical structure of PVDF thin film. After post-heating treatment, the amount of bubble was reduced. This result implies that the DMF solution is almost removed from PVDF thin film, and the PVDF nanoparticles are clearly observed on the surface of PVDF thin film. In FT-IR, the peak intensity at 1669 cm^{-1} for -C=O by DMF solution largely decreases after post-heating, and the post-heated PVDF thin film shows mainly two crystalline phases (α and β phases), which represents the peaks at 975 and 1402 cm^{-1} for α-phase and the peak at 1072 cm^{-1} for β-phase, respectively. The formation of two phases (α and β phases) attributed to the increment in the dielectric constant of the post-heated PVDF thin film. The capacitance and dielectric coefficient values were measured to be 96 nF and 15 at 1 kHz frequency in post-heated PVDF thin film, respectively. The detailed characteristics of the post-heated PVDF thin film using FE-SEM, FT-IR, XRD, and LCR meter are under study and will be discussed in detail.

TF-ThP-17 The Microstructure, Roughness, and Electrical Properties of v-Doped SiC Films*, **Chao-Te Lee Lee**, W. Chen, H. Chen,* Taiwan Instrument Research Institute, National Applied Research Laboratories, Taiwan

Silicon carbide (SiC) thin film with various V contents were deposited on Si(100) substrate at room temperature by RF magnetron sputtering system using sintered SiC (99.95% purity) and V (99.995 purity) targets. The as-deposited films were annealed in the temperature of 1000 ^{o}C under vacuum in 1 hour. Effects of V-doped and annealing on the composition, microstructure, roughness, and electrical properties of films were examined by field emission scanning electron microscopy with an energy dispersive X-ray spectroscope(SEM-EDX), X-ray diffraction (XRD), atomic force microscopy (AFM), and resistance meter. The XRD and AFM results show that all of the as-deposited films were amorphous with smooth surface. The roughness of the as-deposited films were all below 0.3 nm. After 1000 ^{o}C annealing, only the β-SiC(220) phase was been observed of SiC and $(SiC)_{98.2}V_{2.8}$ films. The β-SiC(100) and β-SiC(220) two phases were been observed of the others annealed films. The roughness of the annealed films were hugely increased with increasing V content when the V content is over 2.8 at.%. The roughness of the annealed$(SiC)_{63.6}V_{36.4}$ film was 9.6 nm. The electrical properties of the annealed films was similar with XRD and AFM analysis. It was demonstrated that the annealed $(SiC)_{1-x}V_x$ film was semi-insulating when the V content was over 28.2 at.%.

TF-ThP-19 Fluorine-Doped SiO_2 Films Applied to Optical Coating Deposited by Reactive Magnetron Sputtering*, B. Liao,* Taiwan Instrument Research Institute, Taiwan*; **Chien-Nan Hsiao**,* National Applied Research Laboratories, Taiwan

Porous SiO_2:Ffilms were deposited by reactive magnetron sputtering with a Si metal target at room temperature. Various ratios of O_2 to CF_4 gas were introduced to deposit SiO_2:F films. The optical properties, microstructure, surface roughness, and crystalline structure, of SiO_2:F films have been studied. The refractive index at 550 nm decreased from 1.46 to 1.39 with increasing CF_4 ratio. Then high reflection coating at 1064nm were deposited with Nb_2O_5 and SiO_2:F as high and low refractive materials.

TF-ThP-20 Low-Density SiOC Thin Films Grown by Low Temperature Plasma-Enhanced Chemical Vapor Deposition for High Performance Acoustic Bragg Mirrors*, **Julian Pilz**, N. Andrianov,* Microsystems Division, Silicon Austria Labs, Austria*; T. Sinani,* Sensor Systems Division, Silicon Austria Labs, Austria*; S. Azeem, T. Dao, M. Moridi,* Microsystems Division, Silicon Austria Labs, Austria*; G. Bruckner,* Sensor Systems Division, Silicon Austria Labs, Austria

Solidly mounted resonators are an important type of bulk acoustic wave resonators, which are applied in devices such as radio-frequency filters. To decrease acoustic losses into the substrate, dielectric Bragg mirrors are applied between the bottom electrode and the substrate within the layer stack. These mirrors typically consist of alternating high (W) and low acoustic impedance (SiO_2) films. To increase the acoustic impedance contrast and thus the performance of the mirror and resonator, one approach is to lower the acoustic impedance of the low acoustic material which depends on the density and elastic modulus. In literature, doping of SiO_2 with C has been shown to be an effective approach to reduce the dielectric function with respect to pure SiO_2.[1]

In this study, plasma-enhanced chemical vapor deposition (PECVD) is investigated for growing low acoustic impedance SiOC (carbon doped silicon oxide) thin films on 100 mm diameter Si wafers with native oxide. SiH_4, CH_4, and N_2O are used as the precursors for Si, C, and O, respectively, and Ar is added as neutral species to the processing plasma. The substrate temperature is varied from 50 °C to 350 °C, the total flow rate at a constant pressure (1.2 Torr) from 174 sccm to 698 sccm, and the CH_4/N_2O flow rate ratio from 0 to 0.2.

Generally, increasing the total flow rate and decreasing the substrate temperature leads to a decrease of the refractive index, which is used as a measure of the density of the film. At 50 °C and a total flow rate of 698 sccm, the refractive index (at 633 nm; spectroscopic ellipsometry) and the mass density (graviometry) can be tuned from 1.37 to 1.42 and 1.6 to 1.9 g/cm^3, respectively, by tuning the CH_4/N_2O ratio, with the lowest values found at CH_4/N_2O=0.08. The RMS roughness (atomic force microscopy) increases (10-20 nm for around 500 nm thickness) and the films become softer with increasing CH_4/N_2O ratio (0-0.2), where the elastic modulus drops by 50 % (nanoindentation). Fourier transform infrared spectroscopy furthermore shows changes in the chemical structure with changing ratio of Si, C, and O bonds.

In conclusion, the study shows the potential of using a low temperature PECVD process for tuning the acoustic impedance of SiOC thin films. As the main knob the CH_4/N_2O flow ratio is investigated which allows to change the chemical and structural properties of the material, supposedly creating a more open structure and weaking the bond strength. In further studies, the films will be tested in a resonator test device and benchmarked against industrial state-of-the-art layer stacks.

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2D Materials Technical Group
Room 303 - Session 2D+AS+BI+HC+SS-FrM

2D Materials: Biological, Electronic, Energy, and Other Applications

Moderators: Robert Hovden, University of Michigan, **Jyoti Katoch**, Carnegie Mellon University

8:20am **2D+AS+BI+HC+SS-FrM-1 Printable Electrochemical Biosensors based on 2D and 3D Graphene***, A. Ebrahimi, **Derrick Butler**, V. Kammarchedu, K. Zhou,* Penn State University **INVITED**

The increasing demand for low-cost and field-deployable biosensors has driven researchers to explore robust and scalable biochemical sensor materials and fabrication strategies. Compared to more complicated and expensive photolithography methods, printing techniques – including inkjet and direct laser writing – can enable tailorable and easily-prototypable sensors that are conducive to testing at the point of need. Electrochemical sensors have the potential to meet these criteria and integrate well with printing methods.[1] In recent years, graphene has emerged as a key material in the area of electrochemical biosensors due to high conductivity, wide electrochemical window, biocompatibility, tunability, and excellent surface sensitivity.[2] In particular, advances in preparation of solution-phase graphene suspensions (such as inks containing 2D graphene sheets) have brought about breakthroughs in printed electronics, while the advent of laser-induced graphene (LIG) has enabled the direct writing and integration of 3D porous graphene patterns in various low-cost substrates.Over the past few years, our group has developed different facile functionalization methods to enhance the sensitivity and specificity of printed devices based on graphene ink and LIG, with special attention to sensor performance in complex biological fluids (such as serum, saliva, sweat).[3,4] We have investigated application of the sensors for *in vitro* detection of small molecules involved in neurological functions, kidney disease, and wound infection as well as real-time monitoring of drug-induced response of cancer cells and biofilm biomarkers. Interfacing of the printed sensors with low-cost readout electronics and smartphone has been also demonstrated to showcase the sensor applicability for remote sensing at the point of need. Convergence of machine learning with electrochemical sensing has been also investigated, demonstrating a significant enhancement of sensitivity, while enabling reliable multiplexing of example biochemical markers in saliva and sweat. This talk will highlight our recent progress and ongoing work on advancing printable graphene biosensors in more detail.

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9:00am **2D+AS+BI+HC+SS-FrM-3 A Large Area Selective Emitter for Thermophotovoltaic Applications***, **Minsu Oh**, K. Grossklaus, D. DeMeo, Z. Kranefeld, T. Vandervelde,* Tufts University

Thermophotovoltaic (TPV) devices enable energy harvesting from waste heat. In a TPV system, photons radiated by a selective emitter are converted into electricity by a photodiode due to the photovoltaic effect. The total photon flux available for power conversion is determined by the temperature, emission spectrum, and size of the emitter. Due to the engineerability of metamaterial's optical properties, they have been widely used to create TPV emitters with a desired emission spectrum for varying heat source temperatures. However, the difficulties in fabricating nano- or micrometer-sized metamaterial features that are two-dimensional over large areas pose challenges to realizing a large emitter. This fundamentally limits the output power of a TPV system due to power density restrictions. Therefore, achieving large area emitters with engineerable optical properties are critical for utility of TPV devices at scale with a reasonable power output. In this work, we experimentally demonstrate a 4-inch diameter selective emitter fabricated from one-dimensionally patterned Si and Cr. The selective emission of the emitter peaks at 3.75 µm, which targets 773K blackbody temperature, with a bandwidth of less than 1.5µm. The emission bands of this structure can also be engineered for varying source temperatures owing to the interference effects. Moreover, due to the fabrication ease, our emitter can easily be scaled up to any size of the substrate. We also present the impact of temperature and oxidation on the emission band when heated up to 1000K.

9:20am **2D+AS+BI+HC+SS-FrM-4 Advanced Two-Dimensional Nanohybrids for Efficient Electrocatalytic Hydrogen Evolution***, **Fei Yao**,* University at Buffalo-SUNY

Hydrogen (H_2) shows great potential in reducing greenhouse gas emissions due to its environmentally friendly nature and high gravimetric energy density. It can be generated via electrochemical water splitting based on the hydrogen evolution reaction (HER). It is well known that Pt-group metals (PGMs) are excellent catalysts for HER, but their broad adoption is limited by high cost and scarcity. Recently, two-dimensional (2D) molybdenum disulfide (MoS_2) is regarded as a promising alternative to PGMs due to its large surface area, rich active sites, and ideal hydrogen adsorption energy. However, its practical application is hindered by the intrinsically low electrical conductivity arising from the semiconducting nature of 2H phase MoS_2. On the other hand, 2D Ti_3C_2 MXene with high electrical conductivity, excellent hydrophilicity, and large interlayer distance has been intensively investigated in energy storage devices lately. Compared with charge-neutral graphene, MXene exhibits a negatively charged surface due to the existence of numerous surface functional groups (-OH, -O, -F, *etc.*), which not only enhances the dispersion of MoS_2 precursors but also promotes MoS_2 nucleation, making it a superior template for MoS_2 synthesis. Nevertheless, undesired oxidation of MXene occurs in aqueous solutions, reducing the overall catalyst stability.

To address the above issues, we employed a one-step solvothermal method using DI water/DMF as bisolvent and constructed a metallic 1T phase-enriched MoS_2/MXene/CNT composite as HER catalyst. A low overpotential (169 mV) and Tafel slope (51 mV/dec) along with the highest turnover frequency (7 s^{-1} at - 0.23V vs. RHE) and an ultralong lifetime (72 hours) was successfully achieved. The origin of the outstanding HER performance of the ternary composite can be ascribed to: (i) the prevention of 2D layer restacking as well as the enlarged surface area due to the 2D/2D MoS_2/MXene integration and ion intercalation; (ii) the vertical growth of MoS_2 flakes on the MXene template which increases the exposure of MoS_2 edge planes, maximizing the total number of active sites; (iii) the synergistically enhanced conductivity because of the formation of hybrid 1D/2D conductive network via the integration of 1T-phase metallic MoS_2, conductive MXene backbone with suppressed oxidation along with the CNT crosslinks, minimizing the charge transfer resistance at the electrode/electrolyte interface. This work demonstrated an effective strategy for two-dimensional material structure-property engineering with the aim of optimizing the HER performance which will shed light on the development of the next-generation PGM-free HER electrocatalysts.

9:40am **2D+AS+BI+HC+SS-FrM-5 Bandstructure Engineering in Two-Dimensional Semiconductors***, **Keun Su Kim**,* Yonsei University, Republic of Korea **INVITED**

The tunable band structure of two-dimensional quantum mater is not only interesting in itself, but also useful for the fundamental study of condensed matter physics. As example, surface chemical doping can be used to reduce the band gap of black phosphorus over the energy range greater than its intrinsic band gap [1]. This could be used to deliberately induce a topological phase transition to a Dirac semimetal phase protected by spacetime inversion symmetry [2]. It could also be used to trace the evolution of quantum phases (pseudospin) order across the topological phase transition [3]. In this talk, I will introduce our recent study on the band renormalizations and pseudogap of black phosphorus doped by alkali metals [4]. Using angle-resolved photoemission spectroscopy (ARPES), we found that the simple quadratic band dispersion of doped black phosphorus anomalously bends back towards zero wavenumber, which can be explained by Anderson-McMillan's framework developed for the band structure of liquid (or disordered) metals in the 1960s. This is a natural consequence of resonance scattering by the potential of dopant ions with short-range order. The depth of scattering potential tuned by different kinds of alkali metal (Na, K, Rb, and Cs) allows us to classify the pseudogap of p-wave and d-wave resonance.

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10:20am **2D+AS+BI+HC+SS-FrM-7 Graphene – Ferritin Interface Unpins Fermi-Level and Induces Temperature Dependent Coherent Tunneling Across Biomolecular Junctions***, **Ayelet Vilan,*** Weizmann Institute of Science, Israel*; N. Kumar Gupta,* National University of Singapore*; S. Kumar Karuppannan,* National Quantum Fabless Foundry, Singapore*; R. Reddy Pasula,* Nanyang Technological University Singapore*; J. Martin, W. Xu,* National University of Singapore*; E. May,* Nanyang Technological University, Singapore*; A. Pike,* Newcastle University, UK*; H. Astier, T. Salim,* National University of Singapore*; S. Lim,* Nanyang Technological University, Singapore*; C. Nijhuis,* University of Twente, Netherlands

Molecular electronics is one road to ultimate miniaturization: can we reduce the size of an electronic element to a size of a single molecule? However, as the size reduces to few-atoms level, it becomes harder to distinguish the role of the molecular core from that of the contacts. Here we show the prominent role of graphene interfaces with Fe storing proteins in the net charge transport across their tunnel junctions. Here, ferritin (AfFtn-AA) is adsorbed on graphene by non-covalent amine-graphene interactions. In contrast to junctions with metal electrodes, graphene has a vanishing density of states toward its intrinsic Fermi-level (“Dirac point”), which increase away from the Fermi-level. Therefore, the amount of charge carriers is highly sensitive to temperature and electrostatic charging (induced doping), as deduced from a detailed analysis of charge transport as a function of temperature. Moreover, increasing the iron loading of ferritin, changes the graphene from n- to p-doping. Remarkably, the temperature dependence can be fully explained within the coherent tunneling regime due to excitation of hot carriers. The sensitivity of graphene (and 2D materials in general) to electrostatic charging opens rich possibilities in employing interface electrostatics in tuning the electronic properties of molecular junctions and is important for 2D / biomolecules hybrids in general.

10:40am **2D+AS+BI+HC+SS-FrM-8 The Influence of Selenium Incorporation on the HER Catalytic Activity of Electrodeposited Se-MoS_x Electrocatalysts***, **Lee Kendall**, G. Zangari , S. Mc,* University of Virginia

With the increase in the global consumption of energy, the need to meet the growing energy demands has put significant pressure on the current means of energy production and storage.To meet this demand, water splitting has seen substantial efforts in developing catalytically active materials that replace costly materials, such as Pt, to allow for economically viable implementations.MoS_2 has attracted significant attention over the past decade due to its low cost and availability. Additionally, MoS_2 is one of the most promising materials for electrocatalytic hydrogen evolution as its Gibbs free energy of hydrogen adsorption, $\Delta G^{H}_{0,ads-}$, is the closest to Pt, a state-of-the-art catalyst, when compared to other metallic materials. However, due to the limited number of accessible edge sites, as well as high kinetic barriers for H_2 evolution, the catalytic performance of MoS_2 is still far from the needed requirements. To address this, researchers have investigated amorphous MoS_x due to its increased structural heterogeneity that increases catalytic site density. Combined with short-range atomic arrangements that enable adequate electronic conductivity, amorphous MoS_x is an attractive candidate for electrochemical processes.This can be further improved, however, as the bridging bonds are the most catalytically active while the terminal and apical are significantly less active.To increase their activity, we investigated incorporating selenium into MoS_x due to the success in crystalline, selenium alloyed MoS_2. This success centered on obtaining a more thermoneutral ΔG^{H}_{ads} for the sulfur edges and basal plane, similar motif to terminal and apical bonds in the amorphous system, respectively.To accomplish this, we used an electrodeposition technique that allows for the incorporation of selenium into the MoS_x polymeric chains. We will report on this investigation of the electrodeposition of Se-MoS_x and its effect on the physical, electronic, and catalytic properties towards the hydrogen evolution reaction. Through electrodepositing catalytically active Se-MoS_x thin films, this effort demonstrates improved HER efficiency over current, low-cost materials.

11:00am **2D+AS+BI+HC+SS-FrM-9 Two-Dimensional Skintronics***, **Dmitry Kireev**, D. Akinwande,* The University of Texas at Austin **INVITED**

Modern healthcare displays a significant shift from hospital-based medicine towards a personalized, ambulatory, and wearable approach. In this regard, the development of skin-wearable electronics (*skintronics*) is an essential step toward mobile health monitoring, the healthcare Internet of Things, and eventually preventive medicine. Continuous long-term monitoring of brain activity, heart activity, body hydration, or temperature, is vital for better comprehension of human physiology, understanding systematic disease risk factors, and building preventative care solutions. In this work, we utilize *graphene* and other *2D materials* such as platinum diselenide ($PtSe_2$) and platinum ditelluride ($PtTe_2$) to construct the thinnest elements of skintronics - electronic tattoos. The $PtSe_2$ and $PtTe_2$ e-tattoos that can be grown at comparably low temperatures (400ºC) were found to have superior sheet resistance and electrode-skin impedance compared to monolayer graphene e-tattoos. On the other hand, we also report on the significant advancement of the classic graphene electronic tattoos by introducing graphene nanoscrolls and stacking multiple graphene monolayers. Moreover, we show that graphene tattoos can be made insusceptible to sweat by introducing microholes into their structure. Significantly, we show that graphene electronics tattoos can be used for deep tissue monitoring, detecting complex analytes such as blood pressure and respiration rate in a continuous and entirely non-invasive manner. Beyond the simple use of graphene tattoos as passive electronic elements, we have discovered that the semimetallic 2D material can be used as transistors, biased electrostatically through the body itself, creating transistor tattoos. The body-gated graphene tattoo transistors can function as biosensors or small-signal amplifiers, contributing to the development of higher-fidelity electrophysiology measurements and decreased susceptibility to movement-related artifacts.

11:40am **2D+AS+BI+HC+SS-FrM-11 Ultrasonic-Assisted Assembly of Metal Nanoparticles within Graphene Oxide for Tailoring Stem Cell Response***, J. Jaiswal ,* Indian Institute of Technology (Banaras Hindu University) , India*; **Marshal Dhayal,*** Indian Institute of Technology (Banaras Hindu University) , India

Recently 2D material-assisted stimulation for cellular functions has gained significant attention. In this paper, we will be presenting the methodology used for preparing tunable properties of 2D surfaces incorporating metal nanoparticles (NP) within graphene oxide sheets. The study will report the use of mechanical forces generated through an ultrasonication-assisted method for increased diffusion of metal ions in graphene oxide (GO). The transmission electron microscopy (TEM) analysis has been used to confirm the distribution of metal particles in GO sheets whereas Raman spectra were used to identify the relative changes in the Raman bands. The study presents a correlation of these observations with corresponding confirmation in the distortion of multilayer assembly of thin layers of GO by the nucleation of metal nanoparticles. The X-ray diffraction (XRD) spectra of GO-NP also demonstrated similar outcomes in Raman spectra. UV-visible spectra and X-ray photoelectron spectroscopy (XPS) analysis were used to determine optical activity and relatively % proportions of their atomic concentrations. These unique combinations of functionally graded GO-NP were used to study the response of human mesenchymal stem cells. This method may be helpful to address the challenges associated with developing metallic assembly within graphene oxide without chemical functionalization of their inert surface for their application in the biomedical field.

AVS Quantum Workshop
Room 301 & 302 - Session AQS-FrM

AVS Quantum Science Workshop

Moderators: Charles R. Eddy, Jr., Office of Naval Research Global - London, UK, **Rachael Myers-Ward**, U.S. Naval Research Laboratory

8:20am **AQS-FrM-1 AQS Workshop Opening Remarks***,*

9:00am **AQS-FrM-3 Electronic Excitations of Defects in Semiconductors – First-Principles Simulations and Quantum Embedding***, **André Schleife,*** University of Illinois **INVITED**

Defects are present in semiconductors both intrinsically and through doping and critically determine the material properties. In particular, their electronic excitations underlie the optical response in many cases and transitions between electronic energy levels are promising for quantum information purposes. Hence, modeling these properties from first-principles is an important research direction of quantum mechanical computational materials science. Total energies and the electronic structure as well as the optical properties are described by density functional and many-body perturbation theory.

In this presentation I will outline the fundamentals of these techniques and illustrate applications to defects in MgO and Al2O3. Results for atomic geometries and optical properties will be compared to experiment for the oxygen vacancy in MgO and various defects in Al2O3. Subsequently, I will discuss recent attempts from the literature to incorporate quantum embedding techniques into solving the electronic structure problem and computing optical properties including excitonic effects.

9:40am **AQS-FrM-5 Break***,*

10:00am **AQS-FrM-6 Running Quantum Circuits on a Neutral Atom Quantum Computer***, **Mark Saffman,*** University of Wisconsin-Madison and ColdQuanta **INVITED**

One of the daunting challenges in developing a computer with quantum advantage is the need to scale to a large number of qubits while maintaining the fidelity and isolation of pristine, few qubit demonstrations. Neutral atoms are one of the most promising approaches for meeting this challenge, in part due to the combination of excellent isolation from the environment and the capability to turn on strong two-qubit interactions by excitation to Rydberg states.

I will present results of running quantum algorithms for preparation of multi-qubit GHZ states, phase estimation with application to a basic quantum chemistry problem, and hybrid quantum/classical optimization. The circuits use a universal set of quantum gates based on microwave and optical control of Cs atom qubits. Two-qubit gates are implemented using Rydberg interactions.

These results on a neutral atom quantum processor are the “tip of the iceberg” relative to what we believe will be possible with further development of the neutral atom approach. Atomic qubits are identical, have excellent coherence properties, and are essentially cost free with no fabrication required. Realizing the full potential of programmable large scale atomic arrays requires solving some outstanding challenges including atom loss due to imperfect vacuum conditions, optical addressing with large space-bandwidth product, high power and low noise control lasers, and crosstalk-free measurements. I will discuss these challenges and point to fruitful directions for future progress.

10:40am **AQS-FrM-8 Unitary Coupled Cluster Ansatz as an Efficient Way to Perform Electronic Structure Calculations***, **Jim Freericks,*** Georgetown University **INVITED**

In this talk, I will review work recently completed on how to use the factorized form of the unitary coupled cluster ansatz as an efficient way to perform electronic structure calculations via the variational quantum eigensolver and its variants. I will describe the universal nature of the factorized form and how the variational principle improves accuracies more than expected from simple error bounds. I will discuss how this quantum computer ansatz compares with the conventional coupled-cluster ansatz and I will discuss how one can trade off measurements for circuit depth to perform calculations on molecules that use very low-depth circuits (with potential implementations on near-term hardware). I will also describe how one can improve the circuit depth for higher-rank factors by incorporating additional ancilla or by using linear combinations of unitaries. I will end with some prospects for the near term in how quantum chemistry calculations are likely to be performed.

11:20am **AQS-FrM-10 AQS Panel Discussion***,*

Each AQS Workshop speaker will participate in this Q&A Session

12:00pm **AQS-FrM-12 AVS Quantum Workshop Closing Remarks***,*

Electronic Materials and Photonics Division
Room 304 - Session EM1+MN+NS-FrM

Piezoelectric, Ferroelectric, and Multiferroic Devices & Microelectronics

Moderators: M. David Henry, Sandia National Labs, **Stephen McDonnell**, University of Virginia

8:20am **EM1+MN+NS-FrM-1 Piezoelectric Adjustable X-ray Optics***, **Susan Trolier-McKinstry,*** Penn State University **INVITED**

Next generation X-ray observatories require lightweight, high throughput optics that maintain a < 0.5 arcsecond resolution. Thin adjustable X-ray mirrors can correct deformations generated from fabrication errors, gravity release, mounting stresses, and thermal variations, maintaining the high angular resolution (< 0.5 arcsecond) and large effective area (> 2 m^2) required for future X-ray missions. This paper describes fabrication of adjustable mirrors for the Lynx X-ray observatory mission concept.Prototype X-ray mirrors were built on either a 400 µm thick curved *Corning EAGLE XG*®glass substrate or on polished Si.In both cases, a Cr/Ir X-ray mirror coating was deposited on the front (concave) side, and an array of 1.5 µm thick radio frequency (RF) sputtered $Pb_{0.995}(Zr_{0.52}Ti_{0.48})_{0.99}Nb_{0.01}O_3$(PZT) piezoelectric thin film actuators on the back (convex) side to enable correction of figure errors.A two-layer metal routing scheme with a polymeric insulator was used to independently address 288 actuators on the mirror. The two-layer metal allows narrow kerfs between actuators and increased actuator density. A chrome-iridium layer was deposited on the concave side to function as the X-ray reflective coating for the films deposited on the convex side.Anisotropic conductive film was used to bond thin flexible copper cables to flat edges of the mirror to interface with external control electronics. Improved stress balancing process was achieved using compressively stressed SiO_2 films deposited on the convex side of the mirror to balance the tensile integrated stress of the actuator array while also matching the film thickness distribution.Finite element methods were used to assess the impact of film thickness distributions on the convex and concave substrate surfaces.The resulting models show peak-to-valley figure errors of 105 nm, well within the 1 µm peak-to-valley dynamic range of the piezoelectric adjusters. In contrast, when stress compensation was done with an iridium mirror film deposited on the front side, the mismatched thickness distribution results in peak-to-valley figure errors over 3 µm.

9:00am **EM1+MN+NS-FrM-3 Oxide and Nitride Ferroelectric Wurtzite Crystals***, **Jon-Paul Maria,*** Penn State University

In the past three years, the demonstration of ferroelectricity in wurtzite-based crystals introduced exciting opportunities to explore and discover new structure-property relationships in novel formulation spaces, and to investigate new integration and device implementations given new process compatibilities. The seminal discovery of ferroelectric $Al_{1-x}Sc_xN$ by Fichtner *et al.* initiated this excitement and was followed by comparable observations of polarization reversal in the structurally similar $Al_{1-x}B_xN^2$ and the $Zn_{1-x}Mg_xO^3$ systems.

In this presentation our group will present recent results that demonstrate the structure-process-property relationships in the B-substituted AlN and Mg-substituted ZnO nitride and oxide systems. The B-substituted materials exhibit square hysteresis loops with polarization values between 150 µC/cm^2 and 120 µC/cm^2 when boron concentrations range between 2% and 15% respectively. Coercive field values fall with additional boron, from 5.5MV/cm to about 5 MV/cm at B saturation. Bandgap values are approximately 5 eV or above in all cases. Material can be prepared between 100 °C and 350 °C with very little difference in electrical properties. W bottom and top electrodes are used in all cases. Capacitors can be prepared down to 50 nm thick before leakage current becomes problematic during low frequency hysteresis measurements. First principles calculations that rationalize the unit cell volume, bond angle distribution, and remanent polarization will be presented.

Comparable results are found in the $Zn_{1-x}Mg_xO$ system. Between 25% and 35% Mg substitution, square hysteresis loops with remanent polarization values above 100 µC/cm^2 are readily achieved. Transmission measurements show bandgap values between 4.0 eV and 4.2 eV in this range. In comparison to AlBN, coercive field values for ZMO are as low as 1.7 MV/cm. As is the case with AlBN and AlScN, sustaining high insulation resistance to arbitrarily low thickness is challenging, the current thinness limit for low-leakage switching is ~ 125 nm. SHG analysis will also be presented for the ZMO system – preliminary measurements suggest values comparable to ferroelectric niobates.

9:20am **EM1+MN+NS-FrM-4 Development and Processing of $Al_{1-x}Sc_xN$ (x<0.40) Films for Resonator and Filter Applications***, **Giovanni Esteves**, S. Yen, T. Young,* Sandia National Laboratories*; Z. Tang,* The University of Pennsylvania*; E. Schmidt, L. Gastian, M. Henry, T. Bauer, C. Nordquist,* Sandia National Laboratories*; R. Olsson,* The University of Pennsylvania

As the development of aluminum scandium nitride ($Al_{1-x}Sc_xN$/AlScN) films continues to be pushed towards higher Sc content, fabricated devices yield insight into the challenges associated with processing while demonstrating increased electromechanical coupling coefficients (k_t^2) over AlN. The addition of Sc into AlN presents film development and fabrication challenges that increase with higher Sc content such as the reduction of abnormal grains (AG), higher compressive stress, and etching. The development of $Al_{0.6}Sc_{0.4}N$ films using a single-alloyed target poses a significant challenge in terms of managing stress and the density of AG. Compressive stress help in reducing the amount of AG density through tuning the Ar/N_2 flow and pressure, but the magnitude of stress needed to achieve a low density of AG exceed -600 MPa. The use of certain metal templates aid in reducing AG density but are not sufficient to achieve AG-free films. Etching AlScN leads to long etch times due to slow etch rates of 25 nm/min and result in sidewall angles of ~74°. Nevertheless, AlScN lamb wave resonators (LWR) have been fabricated to demonstrate k_t^2 over 10%. Additionally, LWR with varying k_t^2 were interconnected to fabricate ladder filter configurations to determine that amount of bandwidth increase that can be achieved over AlN. Though AlScN demonstrates higher k_t^2, that lead to higher bandwidth, pushing this current technology to achieve more desirable metrics requires more stringent process quality.

SNL is managed and operated by NTESS under DOE NNSA contract DE-NA0003525

9:40am **EM1+MN+NS-FrM-5 Formation of Aluminum Scandium Nitride Microelectromechanical Systems Via Etching in Aqueous Potassium Hydroxide (KOH)**, ***Zichen Tang***, *M. D'Agati, R. Beaucejour, S. Sofronici, J. Zheng, K. Kaylan,* University of Pennsylvania*; G. Esteves,* Sandia National Laboratories*; R. Olsson,* University of Pennsylvania

We report on the etch rate of sputter deposited piezoelectric and ferroelectric Aluminum Scandium Nitride ($Al_{1-x}Sc_xN$) thin films in aqueous potassium hydroxide (KOH). Specifically, we report on the vertical etch rate, lateral etch rate, and sidewall angle as a function of the scandium alloying ratio (x), temperature, and KOH concentration. As the scandium alloying ratio is increased, the vertical etch rate in 30% KOH at 45 °C is reduced from > 100 nm/s for AlN to < 4 nm/s for $Al_{64}Sc_{36}N$. The lateral etch rate, however, follows a very different trend, arriving at a minimum values of 0.05 nm/sec for $Al_{88}Sc_{12}N$. This is in contrast to the much higher lateral etch rates observed for both AlN and $Al_{64}Sc_{36}N$ of 2 nm/s. These trends in vertical and lateral etch rate are shown to hold for KOH concentrations from 10 to 30% and etch temperatures from 45 to 65 °C. We show that the etched sidewall angle can be predicted from a combination of the crystal structure and the vertical and lateral etch rates. We report a technique that utilizes the crystal structure and the vertical and lateral etch rates to form vertical (i.e. 90°) sidewalls solely from aqueous KOH etching. The ability to control the sidewall angle is vitally important in the formation of microelectromechanical systems (MEMS). We report on several piezoelectric MEMS devices fabricated utilizing the KOH etching processes. Finally, we report on the etching of AlScN as a function of ferroelectric polarization.

10:00am **EM1+MN+NS-FrM-6 Interface Reactions During the Ferroelectric Switching of HfZrO Thin Films on InAs**, *A. Irish, Y. Liu, R. Atle, A. Persson, R. Yadav, M. Borg, L. Wernersson,* ***Rainer Timm,*** Lund University, Sweden

Traditional MOSFET-based electronic components have reached severe bottlenecks regarding data handling speed and power dissipation. A very promising alternative approach builds on MOS material stacks with thin ferroelectric oxide films in novel device architectures for e.g. steep-slope transistors, neuromorphic networks, or in-memory computation [1]. $Hf_{1-x}Zr_xO_2$ (HZO) films grown by atomic layer deposition are widely used in this context, due to their excellent film quality and conformity with existing semiconductor technology. Ferroelectric MOS devices based on III-V semiconductors are especially promising for high-speed applications due to the high charge carrier mobility of e.g. InAs. Furthermore, InAs/HZO/TiN devices have shown an unexpectedly high remanent polarization of the ferroelectric film [2]. In spite of the excellent electrical performance, only little is known about the structure, chemical composition, and switching dynamics of the semiconductor-ferroelectric oxide interface. We have previously used X-ray photoemission spectroscopy (XPS) to investigate interfaces of ferroelectric HZO [3], but *in situ* structural characterization obtained during the ferroelectric switching has been lacking until now.

Here, we present operando hard X-ray photoelectron spectroscopy (HAXPES) results from ferroelectric InAs/HZO/TiN MOS devices obtained during electrical biasing and switching. We observe an interface layer consisting of In- and As-oxides at the InAs/HZO interface. As 2p and In 3d core level spectra were obtained after subsequent switching processes of a “positive-up-negative-down” (PUND) series, showing a reproducible increase of the amount of interface oxide upon upward polarization and a decrease upon downward polarization. Thereby, electrical PUND cycles confirm the ferroelectric nature of the MOS device. Such a redox reaction at the semiconductor-oxide interface upon ferroelectric switching has – to our knowledge – not been reported before. Furthermore, we observe that the major fraction of the applied bias does not drop over the 10 nm thin HZO layer, but instead over the thin InAs-oxide interface layer.

These observations are challenging the established understanding of ferroelectric behavior in thin oxide films and are a key to understanding the superior performance of III-V/HZO based devices.

[1] M. Park et al., MRS Commun. **8,** 795 (2018).
[2] A. Persson et al., Appl. Phys. Lett. **116**, 062902 (2020).
[3] R. Athle et al., ACS Appl. Mat. Int. **13**, 11089 (2021).

10:20am **EM1+MN+NS-FrM-7 The Effect of Hf Doping on Piezomagnetic Properties of FeCo for Magnetoelectric Heterostructure Devices*,*** ***Thomas Mion****, K. Bussmann, M. Staruch, P. Finkel,* US Naval Research Laboratory

New developments in magnetoelectric devices have demonstrated increased energy efficiency and temperature stability with reduced size compared to current technologies. Artificial magnetoelectrics, built on the combination of ferromagnetic magnetostrictive materials structurally coupled to piezoelectric and ferroelectric materials, display the ability to control magnetic properties of the ferromagnet with electric voltage across the piezo/ferroelectric layer. The best performance requires the implementation of soft magnetic materials with large magnetostriction and large voltage-induced strain in the piezo/ferroelectric layer. Processing requirements for device fabrication often complicate the realization of these combined qualities as inherent stresses from the deposition technique are often detrimental to the magnetoelectric functionality. Solutions to these problems are rarely reported though alloying of FeCo and subsequent metalloid substitutions such as $(Fe_{0.5}Co_{0.5})_{1-x}C_x$, and $(Fe_{0.5}Co_{0.5})_{1-x}B_x$, have proven successful in reducing the coercive field while retaining high magnetostriction and piezomagnetic properties **[1,2]**.

In this work we present the systematic study of sputter-deposited Hf-doped $Fe_{50}Co_{50}$ alloy thin films with a focus on the correlation between film stress and magnetic softness and find an inflection point from tensile to compressive stress with increasing Hf composition. Scanning electron microscopy (SEM) and X-ray diffraction (XRD) of the $(Fe_{0.5}Co_{0.5})_{1-x}Hf_x$ system reveal the magnetic softening is also correlated to emergence of an amorphous phase with reduced grain size for these sputter-deposited films. We will show the utilization of this new alloy in a multiferroic MEMS resonator device demonstrating a high magnetoelectric response required for magnetic sensors.

[1] Phys. Rev. Applied 12, 034011 (2019)

[2] Appl. Phys. Lett. 91, 182504 (2007)

Electronic Materials and Photonics Division
Room 304 - Session EM2-FrM

Advanced Devices & Fabrication Methods

Moderators: Parag Banerjee, University of Central Florida, **Bryan Wiggins**, Intel Corporation

10:40am **EM2-FrM-8 Two-Dimensional Steep-Slope Transistors Using Graphene Cold Sources***, M. Liu, H. Jaiswal, S. Shahi, S. Wei, Y. Fu, A. Chakravarty, A. Cabanillas, A. Ahmed, F. Yao,* ***Huamin Li,*** University at Buffalo

Two-dimensional (2D) steep-slope field-effect transistors (FETs) with low energy consumption have been considered to have great potential to continue the future exponential growth of semiconductor electronic devices. The performance of conventional 2D transistors is limited by “Boltzmann tyranny” which generates a relatively long thermal tail in energy distribution and limits the subthreshold swing (SS) at 60 mV/decade at room temperature. To break the limit of 60 mV/decade SS, tunneling FETs (TFETs) and negative capacitance FETs (NCFETs) have been proposed, yet they suffer a variety of challenges and issues. Here we investigate an emerging concept of the steep-slope transistors known as cold-source FETs (CSFETs) or Dirac-source FETs (DSFETs) where graphene (Gr) serves as the Dirac source to provide the cold electrons with a localized electron density distribution and a short thermal tail at room temperature, as shown in Fig. 1. For the CSFET with monolayer MoS2 as the 2D channel, the transport factor can be reduced due to the localized electron density distribution and a shorter thermal tail, giving rise to a minimum SS of 29 mV/decade at room temperature, an excellent on/off ratio (~107), and a record high sub-60-mV/decade current density (~4 μA/μm) which are comparable to current steep-slope technologies, as shown in Fig. 2. Similarly, the CSFET with a multilayer WSe2 channel also shows a sub-60-mV/decade SS, as shown in Fig. 3. The 2D MoS2 and WSe2 CSFETs in this work are benchmarked with the 14 nm Si-based FinFET CMOS technology, as shown in Fig. 4 (a). The sub-60-mV/decade SS as a function of drain current (JD) was compared with other steep-slope transistors, including TFETs, NCFETs, and one-dimensional (1D) CSFETs based on a variety of channel materials, as shown in Fig. 4(b). Our work demonstrated the 2D CSFETs as a steep-slope transistor concept for energy-efficient beyond-CMOS technology.

11:00am **EM2-FrM-9 High Performance, RF Interposer Fabrication on Glass with 3 Metal Layers and Embedded TGVs**, *S. Herrera, A. Ruyack, S. Lepkowski, M. Hirabayashi, M. Powner, C. Nordquist,* ***Matthew Jordan,*** Sandia National Laboratories

We will show the fabrication of a 3-metal layer, low-k dielectric, interposer on glass capable of supporting RF and optoelectronic microsystems. Multi-chip modules (MCMs) allow for the combination of several disparate technologies, like wide bandgap MMICs (monolithic microwave integrated circuits) and CMOS mixed signal electronics, in one package. However, wirebond compatible MCMs suffer from long interconnect lengths as well as require many of the passive RF circuit components to be either incorporated on-chip (a loss of active space) or on the printed circuit board (increasing manufacturing complexity). In fact, much of the footprint of a typical RF chip is devoted to passive components such as decoupling capacitors and impedance matching networks. Disaggregating RF circuit components from transistor technologies through repeatable methods of interconnecting RF chips will reduce on-chip real estate leading to decreased cost. Removing components from the circuit board decreases the manufacturing complexity, as well as size, weight, and power. Therefore, an intermediate interposer that both improves upon MCM performance and reduces cost is an attractive solution.

The interposer approach discussed in this presentation utilizes a flip-chip method to electrically connect die, resulting in repeatable connections between the interposer and the die. This differentiates the approach from similar RF interposer methods like the HRL MECAMIC process in which die are embedded in the interposer[Herrault2020]. Integrated passive devices on the interposer include metal-insulator-metal capacitors, resistors, and inductors which further simplify RF integrated circuit chip design.

SNL is managed and operated by NTESS under DOE NNSA contract DE-NA0003525

11:20am **EM2-FrM-10 Single Step Fabrication Process of Alignment Markers for Direct-Write Electron Beam Lithography in Metal-Organic Negative Tone Resist**, ***Guy DeRose,*** California Institute of Technology

Alignment markers, also referred to as fiducial marks, are commonly made by a process called liftoff. In the liftoff process, a bilayer electron beam resist, such as polymethyl methacrylate (PMMA), is spun and baked onto the substrate, then written by the electron beam pattern generator. Following the development of the resist, a metallization step, typically electron beam evaporation, takes place, followed by soaking the coated substrate in a solvent such as N-Methylpyrrolidone (NMP) during which the metal that is not stuck to the substrate “lifts off” and leaves behind the alignment markers of interest. While a standard process, there are many steps involved, and it is possible that the evaporation process might not be compatible with subsequent steps in the fabrication.

Previously we have demonstrated a negative tone resist that is comprised of a metal-organic material [1]. Using electron beam lithography, we have shown that it can produce high fidelity patterns of 15 nm half pitch. To build upon this work, we demonstrate the fabrication of the alignment markers by directly writing them into this resist in a single process step. Due to the fact that the resist contains chromium metal it was hypothesized that the metal content may be detected by the secondary electron detector (SED) has the metal would produce higher contrast. It can be seen from X-ray photoelectron spectra (XPS) of Figure 2 that the resist has reduced into a metallic oxide material to form CrO_x after it has been exposed by the electron beam; this means that the resist material is no longer soluble in the developing solvent, hence a pattern can be formed. The material can also be used as alignment markers because the density contrast between the silicon and the CrO_x material is dramatically increased by a factor of ~2.25 and this inherently increases the effective atomic number contrast which allows them to be detected by the SED, which can be seen by the Monte Carlo simulations of Figure 3. Figure 4 shows the results of writing an array of 20 um square alignment marks, which are commonly used for multi-layer electron beam lithography.

It can be seen by the SED that the pattern shows high pattern quality. We have demonstrated this at 20 KeV, however, we will present the results of using these patterns as alignment markers for direct-write electron beam lithography at 30 KeV and 100 KeV, along with detailed Monte Carlo simulations that describe the interaction between the incident electron beam and the resist/substrate combination.

11:40am **EM2-FrM-11 Non-Destructive Metrology Techniques for Characterizing a-C Hard Mask Films in 3D NAND Structures**, *P. Mukundhan,* ***G. Andrew Antonelli,*** Onto Innovation

Growth in 3D NAND is driven by data-intensive applications that have changed the paradigm for manufacturing to achieve vertical scaling. One of the key steps in the process is the use of hardmask deposition to etch deep, high-aspect ratio features that conventional photoresist cannot withstand. Amorphous carbon (a-C)-based hard masks, grown using plasma-enhanced chemical vapor deposition (PECVD) have been adopted in high volume manufacturing.

Depending on the process condition, these films exhibit a wide range of hardness, electrical resistivity, optical transparency, and chemical inertness. The information needed during design of the material includes thickness uniformity, characterization of optical constants, density, elastic modulus, and bonding structure. The sp^3-to-sp^2 hybridization ratio and the H content determine the thermomechanical properties of the films. Given the complex nature of an a-C system, no single metrology technique provides all the relevant information needed for process tuning.

In this paper, we present results from two non-destructive techniques: picosecond ultrasonics (PULSE™) and FTIR for the qualification of next generation of advanced hard mask materials. A design-of-experiments (DOE) skew (~3µm a-C thickness target) covering different deposition temperature, pressure and time were generated. With the transition of a-C to thicker and more graphitic (opaque) films, the PULSE™ technique is uniquely qualified for measuring thickness and elastic modulus of these films. Results from the systematic study of different types of films demonstrated sensitivity to process variation and excellent correlation to cross-section microscopy. A second set of a-C films in the 0.2 µm -2µm thickness range was generated to test sensitivity to different processes and provide information regarding the bonding characteristics. Studies have shown the correlation between structural characteristics and the etching characteristics which is primarily determined by the sp3/sp2 ratio. Wafer maps have been collected using an Element™ 300mm automated FTIR. We observed that the absorbances for the sp^2 C=C and the sp^3 C-H_x stretching bonds were significantly different and could be used to discriminate the processes. Furthermore, the sp^2/sp^3 ratio was successfully calculated for all samples. Current efforts are focused on finding correlation between the two metrology techniques and their application in etch process optimization for high volume manufacturing.

Plasma Science and Technology Division
Room 305 - Session PS1+MS+SS-FrM

Modelling of Plasmas and Plasma Driven Processes, and Plasma-Surface Interactions II

Moderators: Tetsuya Tatsumi, Sony Semiconductor Solutions Corporation, Japan, **Yu-Hao Tsai**, TEL Technology Center, America, LLC

8:20am **PS1+MS+SS-FrM-1 Helium and Hydrogen Plasmas Interaction with Si-Based Materials for Advanced Etch Applications: Insights from MD Simulations**, ***Emilie Despiau-Pujo,*** *V. Martirosyan, F. Pinzan,* Univ. Grenoble Alpes, CNRS, LTM, France*; F. Leverd,* ST Microelectronics, France*; O. Joubert,* Univ. Grenoble Alpes, CNRS, LTM, France

Featuring ultrathin layered materials in complex architectures, advanced nanoelectronics structures must be etched with a nanoscale precision and a high selectivity to preserve the electronic properties of active layers. Plasma-induced damage and reactive layers formed during the etch process must thus be carefully controlled, a challenge which cannot be addressed by conventional continuous-wave plasmas.To achieve uniform and damage-free etching, one possible route is to use sequential ion modification and chemical removal steps. In the first step, the material to be etched is exposed to a hydrogen (H_2) or helium (He) CCP or ICP plasma; in a second step, the modified layer is selectively removed by wet cleaning (HF bath) or exposure to gaseous reactants only (eg. NF3/NH3 remote plasma). In this paper, Molecular Dynamics (MD) simulations are performed to study the interaction between He and H_2 plasmas with Si, Si_3N_4 and SiO_2 materials. The objective is to better understand the light ion implantation step, and clarify the influence of the ion energy and ion dose on the structural and chemical modifications of the surface. Simulations of low-energy (15-200 eV) He^+ and H_x^+ bombardment lead to a self-limited ion implantation, followed by the formation of a modified layer of constant thickness at steady state. The modified layer thickness increases with the incident ion energy and only few sputtering is observed in the ion energy range considered here. The detailed structure of the modified materials at steady state will be discussed and compared during the presentation. Simulation predictions will also be confronted to experimental results of He^+ and H^+ implantation of Si_3N_4 and SiO_2 layers, followed by HF wet cleaning.

8:40am **PS1+MS+SS-FrM-2 Efficient Parametric Nonlinear Model Reduction of Low Temperature Plasma Applications***, **Abhishek Verma,*** Applied Materials Inc.*; K. Bera, S. Rauf,* Applied Materials, Inc.

Low temperature plasma simulations are playing an increasingly important role in system discovery, design and decision making in industrial applications, with greater demands for model fidelity. Often, high fidelity simulation models necessitate fine spatiotemporal resolution, coupled multiphysics etc., leading to higher computational cost. This precludes the integration of such models for many important scenarios where the models are required to be simulated very rapidly and multiple times. To overcome this challenge, we present a deep learning based non-linear model order reduction method used to develop surrogate models for low temperature plasma applications. We propose a computationally practical approach for model order reduction that is non-intrusive and purely data driven in nature, using convolutional autoencoders and recurrent neural networks from deep learning. Our numerical experiments on radio frequency powered capacitively coupled plasmas shows that deep learning-based model can learn an efficient latent space representation of spatial and temporal features of plasma dynamics. The learning data is generated by the full order model that includes continuity equations for charged and neutral species, drift-diffusion approximation for electron flux, momentum conservation equation for ions coupled with Poisson's equation. The proposed method is extended to parametric model by embedding parametric information into the latent space for broader applications. Finally, we demonstrate the effectiveness of proposed approach over linear-subspace method for low temperature plasma applications.

9:00am **PS1+MS+SS-FrM-3 Novel Approaches to Generate Missing Data for Plasma Chemistry Modelling** *, **Sebastian Mohr,*** Quantemol Ltd., UK*; M. Hanicinec, A. Owens, J. Tennyson,* University College London, UK

Plasma simulations are a standard method in both industrial and academic settings to optimise plasma processes and gain a better understanding of the underlying physical and chemical processes. To get useful results, comprehensive and reliable data on chemical processes in the plasma are vital. These usually need to be collected from multiple sources including journal articles. To shorten this process, several centralised plasma chemistry databases were collected in recent years. The Quantemol-DB database [1] started as simply a collection of reaction data. Since then it has been enhanced by tools to quickly collect and test data for specific gas mixtures such as an automatic set generator and a global model. Here, we introduce new additions to this tool set.

While for some commonly used gases such oxygen or CF4, vast data on heavy particle reactions are available, they are missing for more exotic or newly used gases. In such cases, reactions are usually included by analogy to known gases, including the rate coefficients for these estimated reactions. However, the rate coefficients can actually differ significantly for similar reactions between different molecules. This is especially true for neutral-neutral reactions which can have a significant influence on the chemical composition of the plasma. *Ab initio* calculations are very time-intensive if possible at all, so to get better estimates of missing rate coefficients, we developed and tested a machine learning regression model [2] which gives rate coefficients for binary heavy particle reactions based on fundamental physical and chemical properties of the reactants and products.

Apart from reactions between particles, radiative transitions of excited states also play an important role in plasmas. They determine the density of excited states and provide the flux of photons to surfaces which might induce additional surface reactions. Furthermore, optical emission spectra are an important diagnostic to obtain plasma parameters. In order to incorporate radiative transitions into our set generation tools, we have created a new database of atomic and molecular lifetimes called LiDa which is linked to QDB and enhances our global model to allow for excited state lifetimes. In due course we will also provide plasma emission fluxes.

[1] Tennyson et al., *Plasma Sources Sci. and Technol.***26**, 055014 (2017)

[2] https://github.com/martin-hanicinec-ucl/regreschem

9:20am **PS1+MS+SS-FrM-4 Particle-in-Cell Modeling of Electron-Beam Generated Low Electron Temperature Plasma***, **Shahid Rauf,*** Applied Materials, Inc.*; D. Sydorenko,* University of Alberta, Canada*; S. Jubin, W. Villafana, S. Ethier, A. Khrabrov, I. Kaganovich,* Princeton University Plasma Physics Lab

Plasmas generated using energetic electron beams are known to have low electron temperature and plasma potential, attributes that are particularly useful for atomic-precision plasma processing. [1] It has been demonstrated that electron beam plasmas cause significantly lower degradation of single layer carbon nanotubes than conventional radio-frequency plasmas. [2] In addition, they have been used to etch materials with atomic precision. [3] Electron beam produced plasmas are typically confined using a static magnetic field and operated at low gas pressures. Previous hybrid modeling of these plasmas confirmed that plasma transport can be non-classical in this parameter regime. [4] The electron transport coefficients were empirically tuned in this hybrid model using experimental measurements, and this hybrid model is only expected to be valid over a narrow range of gas pressure and magnetic field. A self-consistent 2-dimensional particle-in-cell model of electron beam produced plasmas is described in this paper. The model examines the creation and evolution of plasma in low pressure (10 – 40 mTorr) Ar gas on injection of an energetic electron beam (2 keV). Low frequency waves are initially observed as the plasma forms and expands across the magnetic field. These waves radiate outwards from the beam axis towards the chamber walls. The waves gradually disappear as the plasma fills the chamber volume. The final steady-state plasma is well-confined by the magnetic field with the plasma more constricted around the beam axis at lower pressure and higher magnetic field. The electron temperature is less than 1 eV for the range of conditions examined. Physical and energy transport in the plasma (i.e., ambipolar diffusion and thermal conduction) are observed to scale differently with magnetic field and gas pressure. The charged species density is, for example, found to be more confined near the electron beam axis than the electron temperature. The effect of gas pressure, magnetic field and beam current are examined in the paper. The impact of these parameters on electron density, plasma potential and electron temperature are found consistent with probe-based experimental measurements. [4]

[1] Walton *et al.*, ECS J. Solid State Sci. Technol. 6, N5033 (2015).

[2] Jagtiani *et al.*, J. Vac. Sci. Technol. A 34, 01B103 (2016).

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9:40am **PS1+MS+SS-FrM-5 Modeling Edge Effects in Wafer Etching with VSim***, **Daniel Main**, J. Cary, T. Jenkins,* Tech-X Corporation

Plasma processing chambers for the etching of wafers are often used to create a uniform etch along most of the wafer. In such a chamber, a plasma is created using a RF source via Capacitive Coupling (CCP) or Inductive Coupling (ICP). The source region is often far from the wafer (thousands of electron Deybe lengths) so that the plasma is nearly uniform for most of the chamber.Therefore, the physics that requires a kinetic approach occurs near the wafer (within a few hundred Debye lengths).An important part of the process is the acceleration of the ions due to the sheath that forms near the wafer. However, the discontinuity in the boundary near the edge of the wafer leads to a non-uniform sheath and hence non-uniform ion velocities impacting the wafer.One way to make the sheath more uniform is to place a "focus ring" (FR) near the wafer edge. To model the essential physics near the wafer, including the effect of the FR on the sheath dynamics, we have used the electromagnetic, fully kinetic, particle-in-cell simulation package VSim.The simulation includes electrons, argon ions and neutral argon gas. We also include collisions between electrons and neutral species, secondary emission off the wafer, and the self-consistent calculation of the electric field, including a proper inclusion of the wafer and FR dielectric constants. Since the electric field is determined by Poisson's equation, including a full kinetic treatment of the electrons is essential for computing the sheath physics, and hence ion dynamics, correctly.Because of the small spatial and time steps required for a fully kinetic model, we include about half the wafer up to the edge and about 200 Deybe lengths above the wafer. We inject both electrons and ions (modeled as drifting Maxwellians) at the boundary opposite the wafer using incoming-flux boundary conditions, which ensure a smooth transition from the assumed infinite plasma reservoir outside the simulation into the simulation domain. We use Rejection-Sampling theory to compute the correct incoming-flux velocities of the injected particles. The boundary that includes the wafer is an absorbing boundary; electrons and ions accumulate on the dielectrics at this boundary. We show that elastic collisions tend to create a more symmetric Ion Angular-Energy Distribution (IAED) function about the normal. Finally, we demonstrate the role the focus ring has on the IAED and sheath dynamics.

10:00am **PS1+MS+SS-FrM-6 A Study on Dielectric Material Etching in Cryogenic Process Based on Atomistic Simulation***, **Junghwan Um,*** Yonsei University, Korea*; S. Cho,* Samsung Electronics Co., Inc., Republic of Korea*; K. Kang,* Yonsei University, Korea

The adsorption of H2, H2O and HF in each membrane was calculated using molecular dynamics and DFT as parameters necessary to know the adsorbate concentration on the surface according to the temperature of SiO2 and Si3N4. After obtaining the parameters for reaction rate of the pathway in which the chemical reaction of each film material appears, the reaction rate according to the surface temperature of the film material was calculated using an analytic model and previously reported experimental results. As a result, the reaction rate according to the surface temperature of SiO2 and Si3N4 was obtained, and the reaction rate increased by decreasing the temperature was presented as a quantitative value. Finally, through the results of this study on the temperature dependence of the surface reaction, the understanding of the cryogenic process was helped, and the overcoming of aspect ratio dependent etching in deep contact was considered.

10:20am **PS1+MS+SS-FrM-7 Machine Learning Based Model for a RF Hollow Cathode Discharge***, K. Bera, A. Verma,* ***Sathya Ganta****, S. Rauf,* Applied Materials, Inc.

Radio-frequency (RF) hollow cathode discharges (HCD) at low to moderate pressures have gained significance for advanced plasma processes in the semiconductor industry. HCDs form in cylindrical cavities in the cathode, and one can use an array of such cavities to create large area HCDs. A neutral-network based reduced order model for HCDs is discussed in this paper, where this reduced order model is trained using results from Particle-in-Cell/Monte Carlo Collision (PIC/MCC) simulations of single hollow cathode holes. In this PIC/MCC model, using charge density of particles, Poisson equation is solved for electric potential, which yields the electric field. Using this electric field, all charged particles are moved. The PIC/MCC code considers particle collisions with each other and with neutral fluid using a Monte Carlo model. RF hollow cathode behavior is simulated and characterized for different hole size, pressure, RF voltage, frequency, and secondary electron emission coefficient. The plasma penetrates inside the hollow cathode hole with increase in pressure, leading to plasma enhancement. The synergistic effect of RF sheath heating and secondary electron acceleration on hollow cathode discharge has been observed. For improved computational efficiency, a reduced order modeling framework has been developed based on neural network using plasma model parameters. Different methodologies have been explored in selecting and preprocessing physical data to train and validate the neural network. The temporal variation of voltage-current characteristics as well as that of spatial profile of plasma variables (density, temperature, etc.) have been used to train the neural network model. The predictions of trained neural network model compare reasonably well with that of the underlying physical model observations in PIC/MCC simulations. The neural network framework is being applied to determine the collective behavior of an array of RF hollow cathode holes for large area HCDs.

10:40am **PS1+MS+SS-FrM-8 Molecular Dynamics Simulations of Plasma-Enhanced Atomic Layer Etching of Silicon Nitride Using Hydrofluorocarbon and Oxygen Plasmas***, **Jomar Tercero,*** Osaka University, Japan*; A. Hirata,* Sony Semiconductor Solutions Corporation, Japan*; M. Isobe, K. Karahashi,* Osaka University, Japan*; M. Fukasawa,* Sony Semiconductor Solutions Corporation, Japan*; S. Hamaguchi,* Osaka University, Japan

Molecular dynamics simulations were performed to study the influence of oxygen (O_2) in the hydrofluorocarbon (HFC) plasma-enhanced atomic layer etching (ALE) of silicon nitride (Si_3N_4). ALE is known to etch a surface with atomic-scale control and precision. Its in-depth understanding is essential for the advancement of fabrication technologies for semiconductor devices. It was presented earlier that such a Si_3N_4 ALE process can lead to an etch stop due to the accumulation of C atoms on the surface [1]. It was then shown that, by introducing an O_2 plasma irradiation step, a stable etch was observed and the etch stop was prevented [2]. In this study, molecular dynamics (MD) simulations were used to clarify the interaction mechanisms of an O_2 plasma with the modified Si_3N_4 surface during the HFC-based ALE process. To do this, CH_2F radicals were used in the adsorption step. It was then followed by Ar^+ bombardment in the desorption step. Subsequently, O_2 plasma was introduced as an additional step to help the removal of the remaining HFC species. This series of steps corresponds to one ALE cycle. Our simulations have shown that, during the desorption step of the first ALE cycle, HFC species assist the removal of the Si and N atoms of the Si_3N_4 by the formation of volatile by-products such as SiF_x, CN_x, and NH_x species. On the other hand, due to the momentum transfer from incident Ar^+ ions, some HFC species were pushed into the bulk layer, forming chemical bonds with Si and N atoms therein. By the addition of the O_2 plasma irradiation step, it was observed that HFC species interact with O atoms adsorbed on the surface. The removal of C atoms was also enhanced by the formation of CO_x. In this way, our MD simulations have shown that the additional O_2 plasma irradiation step prevents the etch stop and allows stable Si_3N_4 ALE cycles.

References

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11:00am **PS1+MS+SS-FrM-9 Understanding Plasma Etch Mechanism of Low-k Materials Under Low Temperature Substrates with Fluorine-Based Precursors***, **Daniel Santos,*** Tokyo Electron America*; C. Vallee,* SUNY Polytechnic Institute, Albany*; P. Wang,* Tokyo Electron America

Plasma etching of ultra-low-k materials at aggressive back end of line (BEOL) nodes has become increasingly challenging as plasma induced damage becomes a significant challenge to overcome. Conventional reactive ion etch (RIE) processes usually occur at a temperature near room temperature in which diffusion of radicals will damage low-k materials surface. Alternatively, to limit diffusion mechanisms and prevent damage, cryogenic cooling of a substrate sub <-100 C can be used. The purpose of this research is to understand how to leverage the range between room temperature and cryogenic temperatures when using fluorine-based plasmas.

For this work we use a 300mm dual frequency TEL CCP chamber equipped with a low-temperature electrostatic chuck to conduct our experiments. Furthermore, we use in-situ OES, ex-situ XPS, and ellipsometry to understand the plasma surface interactions and observe change in etch rates, fluorine content and composition. We find the choice of between different Fluorine molecules plays a critical role in changing the surface fluorination in dielectric materials, and opposite results have been observed. When using NF_3 the etch rate of low-k 3.0 increases from 200 nm min^{-1} at 15C to 350 nm min^{-1} at -40C but the etch rate of thermal oxide remains 10 nm min^{-1} at all ranges between which displays an increase in selectivity between the films. Opposite of that, when using C_4F_8 we observe the etch rate decrease from 135 nm min^{-1} at 15C to 90 nm min^{-1} at -40C with decreasing temperature suggesting that we enter a higher polymerization regime. We have concluded that different temperature threshold can be obtained, for same plasma parameters, for switching from deposition to etching regime and this behavior depends on fluorine molecule and substrate material composition, which also induces a modification of the selectivity. Using this approach, we try to understand the plasma surface reactions for the fluorine molecules as a function of their triple point temperature, surface saturation with F atoms, and condensation mechanisms.

11:20am **PS1+MS+SS-FrM-10 Plasma-Assisted Atomic Layer Etching of Silicon Nitride with Unfragmented Fluorocarbons***, **Chon Hei Lam**, M. Carruth,* University of Texas at Austin*; Z. Chen, J. Blakeney, P. Ventzek, S. Sridhar,* Tokyo Electron America Inc.*; J. Ekerdt,* University of Texas at Austin

The self-limiting behavior in atomic layer etching (ALE) processes promise to deliver atomic scale fidelity for three-dimensional device fabrication. Plasma-assisted ALE processes typically alternate cycles of chemical modification to weaken the surface bonds followed by ion bombardment to remove a limited amount of material. ALE may provide fine control over the etch rate through the “layer-by-layer” process and can limit physical damage to the substrate. Since silicon nitride films are a likely component in self-aligned multiple patterning schemes, we explore silicon nitride ALE by utilizing undissociated fluorocarbon (CF_4 and CHF_3) adsorption followed by argon ion bombardment. The impact of gas precursors, energetic ion energy, substrate temperature, and the nature of the surface chemical modification are discussed. We follow the surface chemistry and monitor structural damage during ALE with various *in situ* probes (X-ray photoelectron spectroscopy and spectral ellipsometry). Using CHF_3 to illustrate surface modification and argon ion bombardment to affect removal in concert with the spectroscopic probes we demonstrate changes to the adsorbed layer during bombardment. The ALE steps are performed at 100 °C (Fig 1). The silicon nitride films were exposed to CHF_3 at 4 mTorr for 60 s in the fluorocarbon adsorption step followed by argon ion bombardment. The F 1*s* peak appears after argon ion bombardment (4 min, 200 eV) at 100 °C. After the first ALE cycle, a C-F bond was detected in C 1*s* spectra at high binding energy (300 eV) (Fig 2a). The energetic argon ions fragment the fluorocarbon and activate the interaction between fluorine and silicon. The ALE process also leads to nitrogen depletion which is shown in the N 1*s* spectra (Fig 2d). After extended ALE cycles, the Si 2*p* peak shifts to higher binding energy and it might indicate that SiO_x and SiF_x formed through the ALE cycles. The intensity of O increases and the intensity of N decreases along the ALE cycles. The fluorine signal was detectable and the signal in C 1*s* spectra was barely noticeable, which suggest fluorine remains after the ALE process and it combines with silicon in the process. The ellipsometry result (Fig 1) shows a consistent removal amount per cycle of 1.4 Å/cycle over the 20 ALE cycles.

11:40am **PS1+MS+SS-FrM-11 Time Resolved Ion Energy Distribution in Pulsed Inductively Coupled Argon Plasma with/without DC Bias***, **Zhiying Chen**, J. Blakeney, M. Carruth, P. Ventzek,* Tokyo Electron America Inc.

Pulsed plasmas have emerged as promising candidates as means for precise control of ion energy/angle dependent surface processes and surface chemistry during plasma process, which are the key to 3nm and beyond device fabrication. The ion energy distribution functions (IEDFs) and ion fluxes over a pulsed period are important to understand as they directly influenced feature profile, damage and selectivity. We have developed an advanced plasma diagnostics (APD) system with advanced pulsing capability, including source, bias and synchronous pulsing. It is a compact inductively coupled plasma system with RF source frequency of 13.56 MHz intended to diagnose the general behavior of biased high-density plasmas. We report the effect of pulse frequency, RF duty cycle and power, DC duty cycle and voltage, and discharge pressure on the IEDFs and ion flux over a pulse period on the APD system. The time-resolved IEDFs and ion flux were measured using a retarding field energy analyzer. The ion energy transitions in a pulsed period from plasma ignition stage to stable stage and from plasma in glow period to afterglow period are studied. The results indicate the ion energy and ion flux are tailored by RF pulsing and RF-DC pulsing. The time-resolved IEDF demonstrates the merits of pulsing to precise control ion energy and flux, and the ion energy spread narrowed by pulsed plasma.

Plasma Science and Technology Division
Room 315 - Session PS2+SE-FrM

Plasma Sources, Diagnostics, Sensors and Control
Moderator: Nathan Marchack, IBM T.J. Watson Research Center

8:20am **PS2+SE-FrM-1 Optical and Electrical Diagnostics of Industrial Plasma Reactors: Measuring the Relevant Physical Quantities to Assist Process Development***, **Gilles Cunge**,* LTM/CNRS-UJF, France*; S. Younesni,* STMicroelectronics/CNRS-LTM France*; N. Loubet, M. Kogelschatz, E. Pargon, C. Petit-Etienne, O. Joubert, E. Despiau-Pujo, N. Sadeghi,* CNRS-LTM, Université Grenoble Alpes, France **INVITED**

As new devices with 3D architectures and new materials are introduced in the microelectronic industry, plasma etching processes are more and more challenged. The necessity to pattern nanometer size features (with high aspect ratio) with an ultrahigh selectivity towards underlayers has pushed the development of new plasma processes with advanced RF power and/or gas injection pulsing schemes. The goal is either to achieve atomic layer etching processes or simply to overcome typical plasma limitations (charging effects, ARDE…etc). However, since the number of different processes possible in a reactor increases rapidly with each new control knob, the development of innovative processes is becoming extremely difficult with empirical approaches (i.e. DOE). It is thus mandatory to get a deep understanding of the impact of knew control knobs on the plasma properties to develop such new processes efficiently, which can only be achieved by using plasma and surface diagnostics. In this paper, we will review plasma diagnostics that are the best adapted to get a clear picture of the impact of the reactor control knobs on the process performances. Plasma diagnostics are separated in two categories: 1) those used to detect radicals (etchants or etch products) with a time resolution of about 1 ms, i.e. modulated beam mass spectrometry as well as spectroscopic techniques such as optical emission spectroscopy, absorption spectroscopy (from the VUV to near IR range) and Laser induced fluorescence. 2) techniques used to measure the charged species with a µs time resolution: specific Langmuir probe for the ion flux measurements in aggressive environment, RFEA for ion energy distribution function and mass spectrometry/RFEA to analyses the ion nature. We will show that it is important to couple plasma diagnostics with surface analysis (e.g. XPS, Raman…etc) to get a clear picture of the mechanisms involved in new processes and illustrate this point with several concrete processes developments in industrial reactors (ranging from pulsed ICP plasmas to downstream processes).

9:00am **PS2+SE-FrM-3 Hole Transport Properties of Nickel Oxide Films Grown via Hollow-Cathode Plasma-Assisted Atomic Layer Deposition***, S. Ilhom, A. Mohammad, M. Niemiec, D. Zacharzewski, P. Chardavoyne, S. Abdari, **Necmi Biyikli**,* University of Connecticut

In contrast to the relative abundance of as-grown unintentionally doped n-type semiconductor materials, there are only a few alternative alloys showing p-type conduction without needing extra high-temperature doping processes. NiO is of particular interest mainly due to its stability and promising performance as hole-transport layers in emerging solar cell device structures. However, to broaden the NiO application domain towards potential back-end-of-the-line (BEOL) transistor devices as potential p-type channel layers, the transport properties of NiO needs to be improved significantly. While low-temperature thermal, plasma, and ozone-assisted ALD efforts have resulted in p-type NiO films with atomic-level precision and large-area uniformity, the hole mobility is far from being sufficient, typically lower than 1 cm^2/Vs.

In this study we have carried out a systematic study on plasma-enhanced ALD (PEALD) of NiO films on Si and glass substrates using nickelocene ($NiCp_2$) and O_2/Ar plasma mixture using hollow-cathode plasma-assisted atomic layer deposition (HCP-ALD). Detailed saturation studies using in-situ ellipsometer monitoring were carried out in the HCP-ALD reactor, scanning for $NiCp_2$ pulse time, O_2 plasma exposure time, purge time, and plasma power. Optimal growth conditions were identified as 90 ms $NiCp_2$ pulse / 5 s purge / 10 s O_2-plasma at 100 W plasma exposure / 5 s purge. 800 cycle runs were conducted to evaluate the substrate temperature impact (100 - 250 °C) on growth-per-cycle (GPC) and film properties.

The resulting p-type NiO films are characterized for their structural, optical, and electrical properties. Films grown at optimal conditions (200 °C) exhibit refractive index values reaching 2.3, which is in good agreement with reported values for the best polycrystalline NiO films in the literature. NiO films deposited on both Si and glass substrates exhibit polycrystalline single-phase cubic structure (*c*-NiO). In order to determine the carrier type and extract field-effect mobility values, we have fabricated vertical NiO/n-Si p-n junction diodes as well as $NiO/Al_2O_3/Si$ thin-film-transistor (TFT) device prototypes to characterize diode I-V behavior and confirm p-type layer structure for NiO, and extract the field-effect carrier mobility, respectively. Our I-V measurement results confirmed p-n junction diode characteristics with decent ON/OFF ratios for forward and reverse diode current values. TFT characterization results as well as detailed temperature-dependent Hall measurements will be used to identify critical hole transport parameters.

9:20am **PS2+SE-FrM-4 In-Situ Measurement of Electron Emission Yield at Silicon Surfaces in Ar/CF4 Plasmas***, **Mark Sobolewski**,* NIST

Plasma simulations require accurate data for the ion-induced electron emission yield at plasma-exposed surfaces. For industrially relevant plasmas, however, direct measurement of yields using ion beams is impractical. In contrast, measurements made in situ, during plasma exposure, provide useful values for the total or effective yield produced by all incident ions. Here, in-situ measurements were performed in an icp system in Ar/CF4 mixtures at 1.3 Pa. The current and voltage across the sheath adjacent to the rf-biased substrate electrode were measured, along with Langmuir probe measurements of ion current density and electron temperature. The measurements are input into a numerical sheath model, which allows the emitted electron current to be distinguished from other currents. The effective yield was determined for thermally oxidized, in-situ etched, and sputter-cleaned silicon surfaces. For thermal oxides in pure Ar, yields agreed with previous measurements [1] on sputtered oxides. By combining measurements made for several mixtures with mass spectrometer data for the relative flux of each ionic species, estimates or bounds were obtained for the individual electron emission yields of the most prevalent ions. [1] M. A. Sobolewski, Plasma Sources Sci. Technol. 30 025004 (2021).

9:40am **PS2+SE-FrM-5 Plasma Characterization: Radical Recombination Sensor Based on Dual Probe Thermopile Heat Flux Sensors***, Johannes Velthuis,* TNO Science and Industry, the Netherlands

Hydrogen radicals play an important role in e.g. the cleaning of EUV reflective mirrors. Therefore there is the need to quantify the surface radical flux in the various (plasma) setups where these effects are studied. In this paper a catalytic radical sensor is presented, based on the measurement of the recombination heat of radicals on a surface, using dual probe thermopile Heat Flux Sensors (HFS). The first HFS1 has a high recombination (probability) coefficient coating, e.g. Pt. The second HFS2 has a low recombination coefficient coating, e.g. Al2O3. Signal subtraction largely eliminates common mode heat losses/gains such as conduction/convection and IR-radiation, the net result representing the radical recombination heat. The signal can be improved by switching the radical source on/off at regular intervals. Radical recombination rates where measured in a remote microwave (MW) plasma chamber (38 Pa H2) over the range 1E18−1E21 atH/(m2s), with nearly linear response as function of plasma power setting. The sensor full scale limit is ~1E23 atH/(m2s) and is dictated by the maximum allowable sensor surface temperature (<250oC).

10:00am **PS2+SE-FrM-6 Dielectric Toroidal Plasma Sources for Improved Plasma Resistance***, Ilya Pokidov,* MKS Instruments

A new sintered alumina toroidal plasma source has been developed that overcomes the limitations that a quartz or hard anodized coated aluminum alloy applicator have. This alumina ceramic applicator is implemented in R*evolution® toroidal remote plasma source (RPS) chassis replacing the quartz, which predominantly is used in photoresist strip by oxygen plasma. The toroidal body is made of 99.5% pure alumina, more resistant than quartz to harsh plasma chemistries, such as H, F and Cl. It can withstand higher ignition and operating voltages, allowing to ignite plasma directly in process gas. Ceramic alumina is a very pure material. Impurities are below 0.5% versus the hard anodized coating typically grown from the base 6061 alloy with impurity content of up to 4.2%. The ceramic extends the principal limitation of quartz in handling halogen and hydrogen plasmas.

The torus is fabricated by first machining two identical halves in green state and then co-firing them together to form a high strength hermetic bond. Afterwards, the alumina torus’ exterior surface is surrounded by a potting compound with high thermal conductivity and low elastic modulus and encapsulated inside a copper cooling jacket to minimize thermo-mechanical stress on the ceramic.

Tests of the alumina ceramic applicator indicate that it can safely operate up to 6kW, full range of R*evolution RPS power without fracturing. Plasma successfully ignited in process gases such as O_2/N_2, H_2, and N_2/H_2 with healthy operating windows. The alumina applicator underwent a 1000-hour life test in forming gas plasma without significant signs of surface erosion. Similar construction methodology is applicable to sapphire. However, a prototype sapphire torus has shown a lower operating power range than the alumina torus.

The paper will present the design methodology to address key technical challenges in the development of a dielectric toroidal applicator for a transformer coupled remote plasma source. Test data will also be presented to demonstrate operating windows and radical output capabilities of the ceramic toroidal remote plasma source in different gas chemistries.

10:20am **PS2+SE-FrM-7 What We Still Won't Know About Plasmas in Simple Diatomic Gases- or Using a DC Glow Discharge in Pure O_2 as an Ideal Test-Bed for Experimental Validation of Models***, Jean-Paul Booth*[1], LPP-CNRS, France **INVITED**

Despite many decades of study, models of discharges in molecular gases still lack accurate data on many key collisional processes, even for such “simple” and ubiquitous gases as O_2. Good data is lacking for near-threshold electron-impact dissociation with neutral products, the role of metastables; of gas heating, vibrational excitation and energy transfer processes; as well as surface recombination and thermal accommodation. Direct measurement of the rate constants of individual processes is a fastidious process, where it is even possible. As an alternative approach, we compare comprehensive measurements of internal plasma parameters to simulations for a plasma with relatively simple chemistry, namely a DC positive column discharge in pure O_2. This well-characterized, stable and uniform discharge is optimal for experiment-model comparison. Although this system has been studied for a many decades, new experimental methods, including synchrotron Vacuum ultraviolet absorption spectroscopy and laser cavity ringdown absorption spectroscopy (CRDS), allow the densities of all the major species (atomic, molecular, in ground and excited states) to be measured, with much-improved absolute accuracy, and with time resolution. The gas translational temperature, and vibrational energy distribution, were also probed. Applied to (partially- and fully-) modulated discharges, these measurements provide unprecedented insight into the kinetic processes occurring, and a profound test of the models. Whereas models can be quite easily adjusted to fit steady state measurements at one given set of operating conditions, trends with pressure and discharge current, and especially the temporal response to current modulation, are much harder to reconcile. In practice, model failures can often be attributed to simple omission of key processes, or to the neglect of their temperature-dependence. If the chemistry studied is simple enough, and the measurements cover all of the principal species (stable molecules in their ground and metastable states, atoms and negative ions) as well as the gas temperature, it becomes possible to identify the missing reactions, and even estimate their rates and activation energies, by adjusting their values in the model to fit the observations. As examples, we have demonstrated that the kinetics of metastable O_2 b molecules cannot be modelled without the inclusion of quenching by oxygen atoms with a significant activation energy. We have also demonstrated the production of ozone by the reaction of O_2 molecules with oxygen atoms chemisorbed on the glass discharge tube walls.

11:00am **PS2+SE-FrM-9 Voltage and Sheath Dynamics in Electropositive Capacitively Coupled Plasmas with Focus Ring and External Circuit***, Yuhua Xiao, J. Brandon, J. Morsell,* NCSU*; S. Nam, J. Lee,* Samsung Electronics Co., Inc., Republic of Korea*; S. Shannon,* NCSU

Capacitively coupled plasmas (CCPs) are widely used in semiconductor processes. The control of plasma to obtain uniform deposition and etching over a large process space is still an open problem, particularly within a few millimeters of the substrate edge. Complex material stacks commonly referred to as focus rings (FR) or process kits are placed at the wafer edge to balance process non-uniformities and provide uniform process to the edge of the substrate. This solution has limitations with regard to process window and eventual material erosion.One promising approach is to combine a focus ring assembly with a tunable external circuit (EC) ground path termination to extend the plasma uniformity to the wafer edge over a wider process space. The effect of FR combined with EC for fine adjustment and minimization of edge process area are presented here. In this work, a simplified FR with EC structure consisting of a variable capacitor and an inductor is adopted to change the impedance between electrodes and the ground, and the sheath voltage distributions and width are modified. Experimental results are measured using hairpin probe, high-voltage RF and DC probes, in-line RF metrology at the powered electrode, and intensified CCD camera imaging of the electrode edge and FR region. The results are further compared to simulations, which use an equivalent circuit model to simulate the effect of this structure on sheath properties. Results show that the FR with EC structure can partially control the DC self-bias and distribute the voltage and the energy loss among different sheaths associated with different electrodes. The EC can affect the sheath dynamics and equipotential lines of the center and near the wafer edge prominently. These results point to possible source design based pathways for engineering the distribution of power dissipation across these sheaths in industrial plasma reactors to improve process performance at the electrode edge.

11:20am **PS2+SE-FrM-10 Time Resolved Diagnostics of a Silver HiPIMS Discharge***, Zachary Jeckell, D. Barlaz, R. Ganesan, D. Kapelyan, K. Martin,* University of Illinois at Urbana Champaign*; W. Huber, B. Jurczyk,* Starfire Industries LLC*; D. Ruzic,* University of Illinois at Urbana Champaign

This work aims to investigate the temporal evolution of a high-power impulse magnetron sputtering (HiPIMS), with a positive cathode reversal, discharge by using the Hiden ANALYTICAL PSM probe, that can measure the ion energies as well as perform charge to mass (q/m) measurements. This allows for time resolved differentiation between the working gas and the sputtered material, which in this case is silver, and enables the quantification of the population of ions at higher charge states. Q/m differentiation allows for the construction of Ag^+/Ar^+, which when combined with previous IEDF measurements can help tailor future depositions to maximize the flux of silver ions. Our previous work studying the time evolution of the IEDF showed the peak energy of the distribution shifts to the set positive pulse voltage within 3 us regardless of conditions, and that there is a clear difference in the distribution during the first 20 us of the cathode reversal and the end of the cathode reversal, which we

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[1] **2019 PSTD Plasma Prize Winner**

attributed to a higher presence of metal ions that are ionized in flight. This work would aim to verify this claim as well as quantify the population of silver in higher charge states. Investigating the population of Ag^{2+}, and other higher level charge states, is of interest because it is believed to lead to film damage for cases of large positive pulse biases, as the energy of the ions will likely be in the etching regime on the HiPIMS structural zone diagram. Multi-ionization results will be compared with fast camera measurements to see if the population of higher order charged states are correlated to the presence of hot spots. The fast camera measurements are taken using the PI-MAX 4 camera with a selected gate width of 100 ns. Additionally, the ionization fraction of silver can be found and the correlation between measured ionization fraction and the deposition rate measured with a quartz crystal microbalance (QCM) can help to determine the fraction of ions that return to the target and self-sputter as well as the fraction of ions that are transported to the substrate.

11:40am **PS2+SE-FrM-11 Title: Curling Probe Analysis for Practical Measurement of Electron Density***, **Daisuke Ogawa**, K. Nakamura, H. Sugai,* Chubu University, Japan

Optical monitoring is a powerful diagnostic tool for plasma processing, but it should be reminded that optical emission from plasma is still secondary information.As learned from a plasma textbook, photon emission results from many electron relaxations of excited species.Behind the relaxation processes, electrons play a role in transferring their energy to create the excited species. The reaction rate of such reactive species strongly depends on electron density and temperature.Therefore, electron monitoring can be a powerful processing diagnostic even in a practical plasma because electron information can be utilized to know radiative and non-radiative species.Aiming for practical use of electron diagnostic, we have developed a curling probe, one of the diagnostics for finding electron density in plasma with a microwave-range electrical resonance.Plasma has a smaller dielectric constant than vacuum, making resonant frequency smaller. The degree of the frequency shift indicates electron density in plasma. The curling probe utilizes the measurement principle, and in particular, the probe utilizes a slot antenna to obtain the resonance.Due to the regulation of the probe space, the antenna is spiral-shaped and configured in a plane.So, the antenna configuration has some unique characteristics, which are not found in other microwave resonating probes, such as a hairpin probe. One of the unique characteristics of the probe is that the probe has a directionality of electron density measurement.We currently consider that the probe enables us to include the probe into an electrode.This configuration is possibly applied to a narrow-gaped capacitively coupled plasma. Our former work showed that the probe is getting ready for practical use because the probe operates under film depositing situations (Ogawa et al., PSST 30 (2021) 085009) with high pressure (<1000Pa). However, the probe still needs to be improved because we have noticed that the probe temperature affects the degree of the resonant frequency shift.We recently measured and analyzed the probe temperature and degree of resonant frequency shift, and found that the resonant frequency shift has a regularity in temperature. The regularity successfully enabled us to calibrate the probe measurement and showed that the probe is ready to utilize temperature-varying situations.This presentation will show our recent progress in electron density measurement with a curing probe under the temperature-varying situation.This presentation will provide an opportunity to discuss how to apply the probe to an industry reactor.

Radiation Effects on Materials Focus Topic
Room 318 - Session RE+AS-FrM
Materials Analysis and Characterization with Radiation

Moderators: Scott Dubowsky, University of Illinois at Urbana-Champaign, **Camilo Jaramillo-Correa**, Pennsylvania State University

8:20am **RE+AS-FrM-1 Characterization of Materials and Surfaces with Various Types of Radiation***, **Zachary Robinson**,* SUNY Brockport **INVITED**

In this talk, I will present an overview of various types of radiation that surface scientists use to characterize materials. In particular, I will focus on my recent work studying materials relevant for post-CMOS neuromorphic computational devices. These materials provide a potential path towards improved power and computational efficiency in a merged biomimetic and CMOS architecture. For this project, we characterized niobium oxides (NbO_2 and Nb_2O_5) using photons ranging from the infrared and visible for quantitative microscopy and spectroscopy through X-rays generated both at synchrotron sources and in benchtop instruments for diffraction and photoelectron spectroscopy. In particular, broad spectrum radiation allows us to study changes in composition and structure brought about in the as-deposited amorphous thin films upon annealing. The various sources of radiation inform our understanding of the material properties by providing information about the crystal structure, stoichiometry, impurities, crystallization percentage, and optical properties. Since undergraduate students were also an integral part of this work, I will describe our efforts in finding ways for them to be productive over a short (8-10 week) summer research internship when using relatively complicated instrumentation.

9:00am **RE+AS-FrM-3 High-Energy (MeV), Heavy Ion Irradiation of Chalcogenide Phase Change Thin Films***, **David Adams**, E. Lang, T. Clark, C. Sobczak, E. Scott, J. Custer,* Sandia National Labs*; T. Beechem,* Purdue University*; K. Hattar, M. Kalaswad, M. Rodriguez,* Sandia National Labs

Phase change thin films continue to attract interest for applications such as non-volatile electronic memory, sensors, and nanophotonics, because the material can be rapidly switched between amorphous and crystalline states accompanied by large changes in electronic and optical properties. In particular, the germanium-antimony-tellurium system remains a benchmark for studies wherein $Ge_2Sb_2Te_5$ has received much attention. In this study, we have evaluated the response of various chalcogenide thin films to high energy, heavy ion irradiation in order to provide additional insight into phase stability. Crystalline $Ge_2Sb_2Te_5$ and $(Ge_2Sb_2Te_5)_xC_{1-x}$ thin films were irradiated with 2.8 MeV Au ions to different doses and characterized subsequently using Raman spectroscopy, X-ray diffraction, thermoreflectance, Transmission Electron Microscopy and 4-point probe methods. Irradiation experiments were specifically designed to induce disorder while avoiding substantial incorporation of projectile species into films therein preserving the as-deposited film chemistry. Specifically, the 2.8 MeV energy was chosen so that ion range > film thickness which leads to less than 0.01 mol.% of projectile species residing within 100 nm-thick chalcogenide films, according to SRIM estimates. Irradiation led to significant changes in both structure and properties. Pure $Ge_2Sb_2Te_5$ thin films were amorphized when irradiated above a threshold dose, ~1e12 cm^{-2}. Both the thermodynamically-stable trigonal and metastable cubic phases were disordered with concomitant changes in electrical resistivity and thermal conductivity observed. Various $(Ge_2Sb_2Te_5)_xC_{1-x}$ [0 < 1-x < 0.12] thin films were also amorphized when irradiated above threshold doses. As with pure $Ge_2Sb_2Te_5$, structural disordering was accompanied by increased electrical resistivity and decreased thermal conductivity. Further insight into collisional-induced disordering was revealed by In-situ Ion Irradiation Transmission Electron Microscopy (I^3TEM). In-situ transmission electron microscopy and electron diffraction mapped the phase-specific response of films confirming different threshold doses for cubic and trigonal phases. Additionally, I^3TEM has been used to study the effects of increasing carbon concentration on phase stability and ion radiation response.

SNL is managed and operated by NTESS under DOE NNSA contract DE-NA0003525.

9:20am **RE+AS-FrM-4 Multiwavelength Raman Microscopy Used to Characterize Surfaces for Plasma-Wall Interaction Study in Tokamaks***, **Cedric Pardanaud**, C. Martin, P. Roubin,* Aix-Marseille University / CNRS, France **INVITED**

Tokamaks aim to study the possibility to produce energy by exploiting hydrogen isotope nuclear reactions. The fusion plasma is confined magnetically, but a cold plasma is in interaction with the inner walls. This plasma-wall interaction, heterogeneous at the scale of the machine can lead to component melting, surface erosion, element migration inside the chamber, dust production, tritium retention, impurity contamination, mixed material formation… These walls were made of carbon in previous tokamaks (abandoned due to formation of thick hydrogenated rich deposits). Inner walls are now composed of tungsten and/or beryllium, presenting good thermal and chemical properties.

I will demonstrate that multiwavelength Raman microscopy is a suitable technique for *post mortem* analyses of tokamak plasma facing components [1]. It delivers an information related to chemistry, which is complementary to the classically used Thermal Desorption Spectroscopy (TDS) and Ion Beam Analyses (IBA). I will focus on analyses of both laboratory made samples and samples collected inside some tokamaks.

I will illustrate my talk by presenting first how Raman, IBA and TDS of amorphous carbon deposits found inside the Tore Supra tokamak compare [2, 3]. Then, I will focus on the defective beryllium system in the JET tokamak [4- 6] and formation of beryllium hydrides [7]. I will finish by presenting some results about tungsten oxides [8, 9].

[1] C. Pardanaud, et al.

Raman spectroscopy and applications, chapter 1, edited by Khan Maaz, Intech (2017)

[2] C. Pardanaud, et al.

Diamond and Related Materials 34 (2013), 100-104

[3] C. Pardanaud et al.

Thin solid films 581 (2015), 92

[4] M.I. Rusu, et al.

Nuclear Fusion 57 (2017), 076035

[5] M. Kumar, et al.

Nuclear Materials and Energy 17 (2018) 295–301

[6] C. Pardanaud, et al.

Physica Scripta 96 (2021) 124031

[7] C. Pardanaud, et al.

Journal of Physics: Condensed Matter, 27 (2015) 475401

[8] Y Addab, et al.

Phys. Scr. T167 (2016), 014036

[9] C. Pardanaud, et al.

Nuclear fusion 60 (2020) 086004

10:00am **RE+AS-FrM-6 In Situ Optical Characterization of High Temperature Defect Kinetics in Mixed-Conducting Oxide Films*, Nicola Perry,*** University of Illinois, Urbana-Champaign **INVITED**

Thin films represent model platforms for the evaluation of new materials for intermediate-to-high temperature electrochemical devices, including electrolyzers and fuel cells. We focus on candidate perovskite-structured mixed- or triple-conducting electrode materials where the bulk mobile ions are oxide ions or protons, and the surface reactions of interest are oxygen reduction/evolution, hydration, and combinations of the two in the form of hydrogenation. Central to their performance is the dynamic defect behavior at temperatures from 300 – 700 °C, particularly the kinetics of defect transport (diffusivities, *D*) and interfacial reactions (surface exchange coefficients, *k*). Conventionally, electrochemical or electrical methods that place precious metal current collectors on the electrode surface are applied to evaluate the ion fluxes; however, we have demonstrated that the presence of such metals actually alters the measured parameters (e.g., *k*) aiming to quantify surface defect kinetics and bulk defect equilibria. Instead, we exploit the coupling between defect concentrations and UV-vis optical absorption to provide contact-free, continuous, and *in situ* evaluation of the films' defect kinetics via isothermal optical transmission relaxation (OTR) responses to step changes in gas-phase chemical potentials. This method has enabled us to observe the evolution of oxygen exchange kinetics during crystallization, where the onset of crystallization corresponds to the initiation of "breathing" by the films, and we demonstrate orders-of-magnitude enhancements in oxygen surface exchange kinetics in films grown by the low-temperature crystallization method vs. conventional high-temperature-grown films. We also have developed a two-dimensional OTR technique to observe defect kinetics across all regions of 1 x 1 cm^2 films simultaneously, of use in cases with spatially heterogeneous responses. We applied this 2D-OTR to model metal | perovskite heterointerfaces to further underline the catalytic effect of metal current collectors on mixed conductors for oxygen exchange and show the surprisingly large spatial extent of that effect away from the interface. Most recently we demonstrated the ability of the OTR method to evaluate hydrogenation kinetics in proton-conducting thin films for the first time, enabling quantitative comparison of candidate new triple-conductor electrodes. Origins and applications of the optical absorption-defect concentration relationship will be discussed.

Funding Source: DOE BES Grant # DE-SC-0018963

10:40am **RE+AS-FrM-8 Exploring the Effects of Radiation on Planetary Surfaces through the Analysis of Experimental Analogs and Returned Samples from the Moon and Asteroids*, Michelle Thompson,*** Purdue University **INVITED**

Materials on the surfaces of airless bodies are continually exposed to the harsh environment of interplanetary space through a process known as space weathering. Space weathering alters the microstructure, chemistry, and optical properties of grains on the surfaces of bodies like the Moon and asteroids. This process is driven by two primary mechanisms: hypervelocity dust impacts, and the interaction of surface material with energetic particles from the solar wind. We can investigate the effects of these processes by performing laboratory experiments and by analyzing materials collected by sample return missions. Samples returned from the Moon via the Apollo missions and from near-Earth asteroids Itokawa and Ryugu by the Hayabusa and Hayabusa2 missions, respectively, have demonstrated that the microstructural and chemical characteristics resulting from solar wind irradiation are complex. Solar wind ions work to vesiculate and amorphize the outer rims (<100 nm) of grains on the surfaces of these bodies, and the depth and degree of this amorphization (e.g., presence and distribution of nanocrystalline domains) varies significantly in relation to the grain composition and its exposure timescale to interplanetary space. Similarly, solar wind radiation can cause preferential sputtering and redeposition, radiation-enhanced diffusion, and/or recoil mixing which can develop atomic-scale chemical heterogeneities on grain rims. We observe such multilayer rims with segregated cation/anion structures in solar wind irradiated silicate minerals from both the Moon and asteroids. In addition, high-energy Fe-group nuclei from solar flares create trails of ionization damage called solar flare tracks. The concentration of these tracks can be used as a proxy for the exposure timescale a grain has experienced on an airless planetary surface. We can further understand these microstructural and chemical characteristics by conducting experiments in the laboratory using ions and energies appropriate for the solar wind. This work has revealed fundamental discrepancies between experimental and natural space weathering, including the rate at which samples amorphize and the development of vesiculated textures. Such results suggest that ion flux, grain composition, and microstructure play a significant role in the development of atomic-scale irradiation characteristics in returned samples. A combined approach of sample analysis and experiments enables us to investigate how solar wind irradiation alters materials throughout the solar system which is critical for building an understanding of the evolution of planetary surfaces through time.

11:20am **RE+AS-FrM-10 Ground-Based Space Environmental Testing of Materials and Components for Spacecraft Mission Assurance*, Sven Bilén,*** *J. McTernan, C. Zawaski,* The Pennsylvania State University **INVITED**

Space presents an extreme environment for spacecraft materials and systems. For example, in the low-Earth-orbit (LEO) space environment, materials and structures are exposed to high vacuum (10^{-4}–10^{-5} Pa), thermal cycling (−150 to 150 °C), ultraviolet light (100–200 nm), space radiation, potential surface impact from micrometeorites and orbital debris (MM/OD), and atomic oxygen (AO). Materials showing promise for future use in space must be assessed and evaluated for their reaction to exposure to the space environment before being baselined for inclusion into critical space infrastructure. Such evaluation can occur via *in-situ* experiments on space vehicles, but such testing is costly, of limited throughput, experiences significant time lags, and provides less specific information to identify points of failure. Ground-based testing of materials and systems under simulated space environmental conditions can address these limitations. Indeed, space hardware, depending on mission assurance requirements, goes through a battery of testing in space-simulation facilities, such as thermal–vacuum, vibration, acoustic, EMI, etc.

Penn State has facilities for full-scale testing of small spacecraft (e.g., 3-U CubeSats) in a LEO–type environment, individual components and materials, spacecraft charging mitigation schemes, and spacecraft–plasma interactions. This facility is comprised of a vacuum chamber capable of thermal cycling through a range of realistic temperatures, a plasma source capable of producing streaming ions (1–4 eV) and low-energy electrons (~0.1 eV), shake tables, anechoic chambers (for EMI testing), outgassing assessment, and radiation (via its Radiation Science and Engineering Center and Breazeale Reactor). This facility is also capable of testing individual components, whose operation is dependent on the plasma environment (e.g., thermionic cathodes, field emitters, plasma diagnostic tools, *in-situ* diagnostics such as Langmuir probes, etc.). System-wide tests that combine multiple tests are beneficial as results can be interdependent. For example, thermal cycling under vacuum that causes outgassing could contaminate sensors or other diagnostic tools such as Langmuir probes. We are working to add atomic-oxygen exposure, increased thermal range, high-energy electron exposure, UV exposure, and simulated MM/OD damage (via short, focused laser pulses) to our capabilities.

Advanced Surface Engineering Division
Room 317 - Session SE+MN+PS-FrM

Nanostructured and Multifunctional Thin Films and Coatings II

Moderators: Jyh-Wei Lee, Ming Chi University of Technology, Taiwan , **Filippo Mangolini**, The University of Texas at Austin

8:20am **SE+MN+PS-FrM-1 New Challenges and Opportunities for Hard and Superhard Coatings*, Aharon Inspektor,*** Carnegie Mellon University **INVITED**

Many hard, superhard and lubricious coatings with superior mechanical properties, thermal stability and chemical resistance are being developed and applied for surface protection in harsh and demanding applications. In this paper we will discuss the status and foreseen trends in PVD hard, superhard and lubricious films.

First, we will review the design of current multifunctional hard coatings and their applications in metal cutting, in automotive and in aerospace industries. Next, we will examine how the Forth Industrial Revolution, a multi-level connectivity of sensors and systems, with "Smart Manufacturing", computer controlled automated facility system, will affect future usage of multifunctional coatings. The talk will conclude with a critical discussion of the resultant challenges and opportunities for next generation of hard, superhard and lubricious coatings.

Surface Science Division
Room 319 - Session SS1+AS+HC-FrM

Oxide Surface Structure and Reactivity

Moderators: Andrew Gellman, Carnegie Mellon University, **Zhenrong Zhang**, Baylor University

8:20am **SS1+AS+HC-FrM-1 Operando Photoluminescence Microscopy Study of Photoreduction of Resazurin on Tio$_2$ Microcrystals*, Hao Zhu,*** *Z. Zhang, W. Lu, B. Birmingham,* Baylor University

Titanium dioxide (TiO$_2$) has been extensively studied for its photo-reactivity-related applications in solar cells, clean hydrogen energy, and environmental remediation. It is commonly accepted that the anatase (A) phase is more photoreactive than the rutile (R) phase. However, the reversed relative photo activities were often reported. In addition, mixed-phase TiO$_2$ has shown the highest photoactivity but the synergetic effect is not clear. Understanding the syngenetic effect at the two-phase interface will lead to a new era of catalyst design.

In this work, operando photoluminescence microscopy was used to investigate the photoreduction of resazurin on anatase microcrystals, rutile microcrystals, rutile (110) single crystals, and anatase (001) single crystals. Our results show that the rate of resazurin photoreduction on the rutile (110) surface was higher than that on the anatase (001) surface. The reaction rates on anatase microcrystals with a large percentage (001) facet are faster than that on anatase (001) single crystals and close to the reaction rate on rutile (110) single crystals. The reaction rate of the anatase microcrystals depends on the morphology and structure of each individual particle. The mechanism of the syngenetic effects at the rutile/anatase interface was also studied on the synthesized A-R two-phase microcrystals.

8:40am **SS1+AS+HC-FrM-2 Unraveling Surface Structures of Ga-Promoted Transition Metal Catalysts in CO$_2$ Hydrogenation*, Si Woo Lee,*** *M. Lopez Luna, S. Shaikhutdinov, B. Roldan Cuenya,* Fritz Haber Institute of the Max Planck Society, Germany

Gallium-containing intermetallic compounds and alloys with transition metals have recently been reported to be active in the hydrogenation of CO$_2$ to methanol. However, the promotional role of Ga in these catalysts is still poorly understood, in particular due to the lack of information about the *surface* structures of the catalysts, especially under reaction conditions. In this respect, studies using surface-sensitive techniques applied to well-defined model systems can provide key information to elucidate the reaction mechanism and provide the basis for the rational design of Ga-promoted TM catalysts.

In this work, we employed *in situ* Near Ambient Pressure Scanning Tunneling Microscopy (NAP-STM) and X-ray Photoelectron Spectroscopy (NAP-XPS), which make possible the studies of surfaces in the reaction atmosphere, to monitor the structural and chemical evolution of the Ga/Cu surfaces in the CO$_2$ hydrogenation reaction. NAP-STM images recorded in the reaction mixture revealed temperature- and pressure-dependent de-alloying of the initially formed, well-ordered c(2×2)-Ga/Cu(111) surface alloy and the formation of Ga-oxide islands embedded into the Cu(111) surface. Thus, NAP-STM studies revealed that the surface undergoes de-alloying and phase separation into Ga-oxide and (1×1)-Cu exposing Ga-oxide/Cu(111) interfacial sites. Notably, in our atomically-resolved STM image on Ga-oxide/Cu(111), it is clearly observed that Ga-oxide grows into an ultrathin oxide layer with $(4\sqrt{3}\times4\sqrt{3})R30°$ superstructure when grown on Cu(111). From NAP-XPS studies on Ga/Cu(111) in the presence of CO$_2$ and H$_2$, the formation of formate was observed, and this intermediate was finally transformed into methoxy at elevated reaction temperatures, the final surface-bound intermediate of methanol synthesis. In contrast to Ga-containing Cu catalyst, on the other hand, there was no reaction intermediate at high temperature on the Ga-free Cu(111) surface, demonstrating that the further reaction does not occur any more from chemisorbed $CO_2^{\delta-}$ on Cu alone. Therefore, the GaO$_x$/Cu interface formed under reaction conditions may expose catalytically active sites, that should be taken into account for elucidating the reaction mechanism on the Ga-promoted systems. For the first time, our *operando* surface characterizations reveal strong evidence that Cu–Ga catalysts are activated in CO$_2$ hydrogenation with the formation of embedded oxide-metal interfacial sites by de-alloying transition, which allow us to prove the promotional role of Ga in Cu-Ga catalysts.

9:00am **SS1+AS+HC-FrM-3 Stabilization of Active Cu Sites on Oxide Surfaces*, Dario Stacchiola,*** Brookhaven National Laboratory **INVITED**

Cu-based catalysts are active for partial and full oxidation reactions. Copper can be oxidized under moderate oxidant pressures and temperature to Cu$_2$O, and further to CuO under typical catalytic reaction conditions. We present here model systems using both copper oxide thin films and single crystals used to interrogate the effect of alkali, metal, and oxide modifiers on the stability of exposed active Cu sites. *In situ* experiments allow the observation of dynamic processes and phases under reaction conditions.

9:40am **SS1+AS+HC-FrM-5 An optimized IRAS Setup to Investigate Adsorbates on Metal-Oxide Single Crystals*, David Rath,*** *J. Pavelec, U. Diebold, M. Schmid, G. Parkinson,* TU Wien, Austria

The IRAS system GRISU (**GR**azing incident **I**nfrared absorption **S**pectroscopy **U**nit) was developed to investigate adsorbates on metal oxide single crystals with maximum sensitivity. GRISU combines the commercially available FTIR spectrometer Bruker Vertex 80v with a UHV chamber [1].

The compact design utilizes only one CF150 flange (6") on the UHV chamber, ensuring the precise positioning of all the optical components and the high-performance requirements.

The system features five mirrors for beam guidance placed in HV and UHV environments and optimizes the system's performance, flexibility, and usability. The result is a small controllable focal-spot diameter (max. 3 mm) on the sample, motorized optical components, and apertures that control the shape of the illumination area on the sample to reduce the background signal. A second aperture limits the incidence angle range of the infrared radiation illuminating the sample. Incidence angles between 49° and 85° are possible.

The simulated system (done with a ray-tracing program and a simplified spectrometer model) shows an efficiency of 13 %, i.e., 13 % of the radiation passing through the first aperture (Ø 6 mm) after the IR source in the FTIR spectrometer reaches the detector after being reflected from the molecular beam spot (Ø 3.5 mm) on the sample. Compared to a commercially available system with two parabolic mirrors with a focal length of 250 mm, the efficiency is about 20x higher.

The performance of the system is demonstrated by first measurements.

[1] J. Pavelec, et al., J. Chem. Phys. 146, 014701 (2017).

10:00am **SS1+AS+HC-FrM-6 Photochemical Fluorination of TiO$_2$(110)*, Melissa Hines,*** *W. DeBenedetti, Q. Zhu, M. Hasany, D. Somaratne,* Cornell University

Fluorine has been widely reported to improve the photoreactivity of TiO$_2$ nanocrystals, but surface science studies of this enhancement have been stymied by the lack of well controlled fluorination chemistries. Fluorine-terminated rutile (110) surfaces were produced by the photochemical degradation of solution-prepared carboxylate monolayers in the presence of XeF$_2$ (g) at room temperature. The reaction initially produces a multi-nanometer-thick surface layer with a nominal composition of TiOF$_2$. The TiOF$_2$ layer largely dissolves with immersion in room temperature H$_2$O, leaving behind a fluorinated surface terminated by 0.8 monolayers of F bound to initially undersaturated Ti atoms. Scanning tunneling microscopy images showed that the fluorinated surface was rough on an atomic scale, displaying short, atomically straight rows parallel to the [001] direction.

The fluorinated surface remained notably contamination free, even after immersion in solution and exposure to air for tens of minutes. The relatively high reactivity of the $TiOF_2$ surface layer towards etching can be rationalized in terms of disrupted charge balance in the surface layer. Consistent with this, density functional theory simulations showed that the removal of bridging O atoms from the fully fluorinated surface to produce O_2 would be exoergic.

10:20am **SS1+AS+HC-FrM-7 Surface Structures of $La_{0.8}Sr_{0.2}MnO_3$ (001) Thin Films***, **Erik Rheinfrank**, M. Brunthaler, G. Franceschi, M. Schmid, U. Diebold, M. Riva,* Institute of Applied Physics, TU Wien, Austria

Lanthanum-strontium manganite ($La_{0.8}Sr_{0.2}MnO_3$, LSMO) is a perovskite oxide used as a cathode material in solid oxide fuel cells, which convert chemical energy to electrical energy. To gain deeper insights into the reaction mechanisms, it is important to understand the structure of the surface at the atomic scale. To this end, we grow atomically flat single-crystalline LSMO thin films on Nb-doped $SrTiO_3$ (STO) substrates via pulsed laser deposition (PLD). Previously, this has been achieved already for the (110) orientation [1,2]. Here, we use a similar approach on the (001) surface that is commonly used for oxide-based electronics and spintronics. The as-grown films were transferred in UHV from the PLD chamber to a surface science system, and characterized with scanning tunneling microscopy, x-ray photoelectron spectroscopy, and low-energy electron diffraction. We show how the LSMO surface structures change due to variation of the oxygen chemical potential upon annealing. Moreover, Ar^+ sputtering and subsequent annealing removes preferentially Mn over La. This can be exploited to transform a B-site (Mn) terminated surface into an A-site (La/Sr) rich surface. The B-site terminated surface is recovered by depositing Mn from an MnO target.

[1] Franceschi et al., J. Mater. Chem. A, 2020, **8**, 22947-22961

[2] Franceschi et al., Phys. Rev. Materials, 2021, **5**, L092401

10:40am **SS1+AS+HC-FrM-8 Adsorption of Organophosphate Nerve Agent VX on the (101) Surface of Anatase Titanium Dioxide***, **Gloria Bazargan**,* NRC Research Associate, U.S. Naval Research Laboratory*; I. Schweigert, D. Gunlycke,* Chemistry Division, U.S. Naval Research Laboratory

We quantify the adsorption of the organophosphate venomous agent X (VX) on the clean and hydroxylated (101) surfaces of anatase titanium dioxide (TiO_2) with density functional theory (DFT) calculations. Our results show that adsorption on the clean anatase (101) surface occurs through the VX phosphoryl oxygen (O=P) site and involves the formation of a Ti⋯O=P dative bond. Steric effects inhibit adsorption through the VX nitrogen and sulfur sites by the formation of Ti⋯N and Ti⋯S dative bonds. On the hydroxylated (101) surface, adsorption similarly proceeds through the VX phosphoryl oxygen site but entails the formation of surface–adsorbate hydrogen bonds. Additionally, weak non-covalent interactions between the surface hydroxyl groups and the adsorbate's nitrogen and sulfur atoms stabilize VX/(101) complexes formed by adsorption through these secondary sites.

Surface Science Division
Room 320 - Session SS2+CA+AS-FrM

Environmental, Atmospheric and Astronomical Surfaces

Moderators: Kathryn Perrine, Michigan Technological University, **Xiao-Ying Yu**, Oak Ridge National Laboratory, USA

8:20am **SS2+CA+AS-FrM-1 Combining Synchrotron X-ray and SFG Spectroscopy Techniques to Illuminate Aqueous Interfaces***, S. Nayak, R. Kumal, A. Carr,* Argonne National Laboratory, USA*; S. Lee,* Argonne National Laboratory*; **Ahmet Uysal**,* Argonne National Laboratory, USA **INVITED**

Chemical separations are central to our energy, environment, and security needs. From efficient refinery and recycling of rare earths to cleanup of contaminated underground waters, chemical separations cover a wide range of processes such as liquid-liquid extraction (LLE), membranes, and sorbents. A common theme in most processes is that the target ions need to adsorb on or go through an interface. Understanding aqueous interfaces at molecular scale, require special experimental techniques that can distinguish the interfacial structures from the overwhelmingly larger bulk.

Surface sensitive synchrotron X-ray scattering and fluorescence, and vibrational sum frequency generation (SFG) spectroscopy techniques are among the most advanced tools available to study aqueous interfaces. Interestingly, these techniques have been developed in separate communities and there are only a handful of studies that take advantage of complementary nature of them. In this presentation, I will summarize our group's efforts in understanding aqueous interfaces in chemical separations, by combining these two experimental techniques. I will provide specific examples where a single method is not enough to decipher the complex interactions at the interface. The examples cover ion-amphiphile interactions in LLE [1-4] and ion adsorption on graphene-oxide thin films [5].

1. Nayak, S.; Kumal, R. R.; Liu, Z.; Qiao, B.; Clark, A. E.; Uysal, A., Origins of Clustering of Metalate–Extractant Complexes in Liquid–Liquid Extraction. ACS Appl. Mater. Interfaces 2021, 13 (20), 24194-24206.

2.Kumal, R. R.; Nayak, S.; Bu, W.; Uysal, A., Chemical Potential Driven Reorganization of Anions between Stern and Diffuse Layers at the Air/Water Interface. J. Phys. Chem. C 2021.

3.Kumal, R.; Wimalasiri, P.; Servis, M.; Uysal, A., Thiocyanate Ions Form Antiparallel Populations at the Concentrated Electrolyte/Charged Surfactant Interface. ChemRxiv 2022, https://doi.org/10.26434/chemrxiv-2022-x8s7x

4.Nayak, S.; Kumal, R. R.; Uysal, A., Spontaneous and Ion-Specific Formation of Inverted Bilayers at Air/Aqueous Interface. Langmuir 2022, https://doi.org/10.1021/acs.langmuir.2c00208

5.Carr, A. J.; Kumal, R. R.; Bu, W.; Uysal, A., Effects of ion adsorption on graphene oxide films and interfacial water structure: A molecular-scale description. Carbon 2022, 195, 131-140.

9:00am **SS2+CA+AS-FrM-3 X-Ray Studies of Extractant and Lanthanide Ion Ordering at Liquid Interfaces Relevant to Solvent Extraction***, **Mark Schlossman**,* University of Illinois at Chicago **INVITED**

Solvent extraction processes are designed to extract a target species of ion from a multi-component aqueous mixture into an organic solvent, then return it to an aqueous phase containing only the targeted species. Ongoing developments of solvent extraction processes are aimed at optimizing the efficiency and kinetics of the separation and recovery of base, rare earth, and precious metals, as well as the reprocessing of spent nuclear fuel and nuclear waste. During solvent extraction, extractants and complexants assist the transport of metal ions across the liquid-liquid interface between an aqueous solution and an organic solvent. Complexation of metal ions with extractants and complexants is believed to take place at or near the organic-aqueous interface, as demonstrated recently by synchrotron x-ray measurements which locate and characterize metal ions and their complexes in the liquid-liquid interfacial region. This presentation will describe recent X-ray studies of model liquid interfacial systems relevant to the extraction of rare earth ions. These results suggest a connection between the observed interfacial structures and the extraction mechanism, which ultimately affects the extraction kinetics.

9:40am **SS2+CA+AS-FrM-5 Probing Surface Chemistry in Complex Environments: Water Disinfectants and Ionic Solutions at the Air/Liquid/Iron Interface***, **Kathryn Perrine**,* Michigan Technological University

Water disinfectants are used to treat pathogens in the water supply, but chlorine is known to react with organic matter to produce toxic disinfectant by-products (DBP). Other disinfectants, such as monochloramine, provide a higher level of disinfection without producing chlorinated DBP's. However, studies have shown that monochloramine can corrode copper and lead surfaces, but little is known for iron-based materials. Iron interfaces are prevalent in soils, minerals, and atmospheric dust, and are known to undergo redox reactions. Iron is a known catalyst in several processes due to its different active sites. Due to the advent of degradation of disinfectants in the water supply, the reaction of monochloramine was investigated on iron interfaces in complex environments.

The interaction of monochloramine was studied at the air/solution/iron interface using *in situ* polarized modulated infrared reflection absorption spectroscopy (PM-IRRAS). These studies are compared with the iron interfaces exposed to aqueous solutions that were used to synthesize monochloramine, $NH_4Cl(aq)$, $NaOH(aq)$, and $NaOCl(aq)$. After exposure to each solution, ATR-FTIR spectroscopy and X-ray photoelectron spectroscopy were used to measure the chemical composition at the interface region exposed to atmospheric O_2 and CO_2 and the region submerged in solution. This builds upon our previous work where we have investigated alkali and alkaline chloride solutions at the air/electrolyte/iron interface. There the anion acts to corrode the surface to produce nucleation sites for carbonate film growth, while the cation influences the mineral film identity and the rate of carbonation from the uptake of CO_2. These findings show that water disinfectants at solution/metal interfaces result in unexpected reactions in complex aqueous systems, which may provide insight for related surface catalytic and environmental processes.

10:00am **SS2+CA+AS-FrM-6 The Surface Chemistry of Martian Mineral AnalogsDuring Triboelectric Charging in Sand Storms***, **Mikkel Bregnhøj**, T. Weidner, K. Finster,* Aarhus University, Denmark

The surface chemistry of the Martian regolith has a significant impact on the atmospheric composition on the Red Planet. For example, methane concentrations vary by a factor of ~3 or more during a Marsian year. Theories based on established photochemical and environmental mechanisms, have so far failed to accurately model the seasonal variation. The currently known gas/solid interfacial chemistry that forms and removes methane from the Marsian atmosphere is insufficient to explain the observed dynamics.

We propose an alternative driver of Martian surface chemistry: wind-driven triboelectric charging of minerals. Sand storms, saltation, and erosion are common phenomena on the Red Planet. In proof-of-principle laboratory experiments, we have shown how Martian mineral analogs can erode each other and induce electric discharges with sufficient energy to (1) ionize and/or dissociate gasses like argon, methane, and carbon dioxide and (2) drive gas/solid interfacial chemistry of organic species present on the surface of these minerals. Using advanced surface spectroscopies (XPS, NEXAFS, etc.) we show how saltation can drastically alter the gas and mineral surface composition. For example, tumbling quartz sand in a methane atmosphere will change the colour of the sand from pristine white to reddish/brown (see attached figure). Using a custom-built container, we also simulate a sand storm with realistic Martian atmospheres and mineral analogs, sealed inside a container made of the very same mineral. In this way, we exclude possible interference effects from the container walls, and come as close to the actual conditions of a sand storm on Mars as is possible on Earth.

10:20am **SS2+CA+AS-FrM-7 Unraveling Water Formation on Planetary and Astrophysical Bodies: The Role of Surface Science***, T. Orlando, **Brant Jones**,* Georgia Institute of Technology **INVITED**

The sources of molecular water in planetary systems is a subject of general interest in astrophysics and astrochemistry and its presence and persistence are critical for life on Earth and for space missions involving long term human exploration.The Moon is the nearest exploration target and sources of water include primordial water, delivery via comets and meteorites, formation and release during small impact events, and solar wind interactions. Our controlled surface science experiments have demonstrated that thermally activated recombinative desorption (RD) or associative desorption (AD) from lunar regolith and other solar wind irradiated grains can be an additional source term for water formation. This involves hydroxyl (-OH) defects made by implantation of solar wind protons. Using several Apollo lunar samples, temperature program desorption (TPD) experiments conducted under ultra-high vacuum conditions yielded first order activation energies for desorption of chemisorbed molecular water and second order activation energies for the RD mediated formation and release of molecular water. Depending on the temperature excursions, RD can occur on a diurnal basis on the Moon and is likely prevalent during impacts with meteorites and meteoroids. This is simulated by laser impact studies followed by state and velocity resolved detection of the photo-produced water. Once formed, the water can either desorb, or be transported on and within the regolith and grain surfaces.Our combined experimental and modeling effort has successfully simulated recent observational data of water on both Mercury and the Moon. Water formation via RD is also likely general under astrophysical conditions that involve proton bombardment followed by thermal excursions (> 400 K), and is critical to the formation of water in star forming regions and in developing strategies for extraction of water for future, sustainable human space exploration missions.

Thin Films Division
Room 316 - Session TF1+PS-FrM
Plasma, PVD and HIPIMS Processes for Emerging and Advanced Materials

Moderators: Joe Becker, Kurt J. Lesker Company, **Christophe Vallee**, SUNY College of Nanoscale Science and Engineering

8:40am **TF1+PS-FrM-2 Growth of c-axis Textured AlN PVD Film on a 2D-MoS_2 Seed Layer***, **Julien Patouillard**,* STMicroelectronics, France*; E. Blanquet, A. Mantoux,* SIMaP, CNRS, University Grenoble Alpes, France*; F. Gianesello,* STMicroelectronics, France*; M. Bernard, S. Cadot, R. Gassilloud, C. Raynaud,* Commissariat à L'énergie Atomique, France

Aluminum nitride (AlN) is a piezoelectric and wide bang gap material which crystallizes in a hexagonal wurtzite structure. This material arouses a certain interest in various fields of microelectronics, in particular radiofrequency (RF) devices [1–3]. Its deposition process is well-known and appears to be reproducible, using either epi-like chemical deposition solutions, or N_2-based physical deposition with Al-target. In particular, AlN deposited by Physical Vapor Deposition (PVD) exhibits a relatively large electromechanical coupling coefficient $k_t^2 \approx 6{,}5\%$. [2]

Due to the lack of bulk AlN substrates and the large lattice mismatch between AlN and silicon, AlN is usually epitaxially grown on sapphire or silicon carbide (SiC) substrates at high growth temperature (≈1000 °C) to achieve higher crystalline quality and hence better device performance [4,5]. However, high cost, limited wafer size or differences in thermal expansion coefficient between AlN and these substrates drastically limit the integration and applications of AlN.

In recent years, the emergence of 2-Dimensional (2D) materials and particularly 2D-Transition Metal Dichalcogenides (2D-TMDs) seems to be a promising approach for the growth of III-nitride. Among 2D-TMDs, MoS_2 is one of the most widely studied materials due to its availability [6,7]. MoS_2 has a natural two-dimensional structure with the sandwich-like S-Mo-S layers serving as building blocks, in which the atoms in the layer are bonded with strong covalent bonding, while the layers are packed together with weak interlayer forces [8,9]. It also presents a hexagonal structure with a close lattice matching with III-nitride (1 % to 3 %) and a chemical compatibility enabling the direct growth of these materials [4,5].

In this presentation, we will demonstrate the direct growth of c-axis textured AlN films deposited by PVD on a well-controlled and uniform MoS_2thin film elaborated by Atomic Layer Deposition (ALD). We will show how 2D materials can be advantageously implemented to improve the texturation of AlN on silicon substrate. Hence, in figure 1, the crystal quality of AlN is assessed by X-Ray Diffraction (XRD) measurements using the Rocking Curve (RC) technique. The FWMH of the omega peak at 18° (Theta 36,04° of (002)) gives a direct information on the mosaicity of the AlN layer. AlN Growth on 2D-MoS_2 seed induces a strong reduction of FWMH compared to Si-based substrate, indicating the preferential reorientation of the AlN matrix along the (002) axis, perpendicular to the substrate surface. This orientation is expected to boost the piezoelectric coefficient, which opens new field of applications on Si substrate.

9:00am **TF1+PS-FrM-3 Synthesis and Hardness of Thin-Film High-Entropy Transition Metal Ceramics***, **Nathaniel McIlwaine**,* The Pennsylvania State University*; M. Hossain,* Pacific Northwest National Lab*; J. Maria,* The Pennsylvania State University

High entropy carbides (HECs) are single phase, multicomponent materials that possess a high degree of configurational entropy on cation lattice sites and can possess enhanced thermal and mechanical properties compared to binary transition metal carbides. Group IIIB, IVB, VB, and VIB transition metal HECs with high hardness and high melting temperatures are prospective materials for refractory applications such as advanced armor, cutting tools, and spacecraft thermal protection systems.

HECs are chemically disordered crystals containing components inclined to form ternary solid solution compounds and carbon deficient phases. Multicomponent carbides produced by conventional reactive sputtering techniques, such as radio frequency (RF) and direct current (DC), are hindered in overall film quality due to uncontrolled microstructure and stoichiometry. This work is focused on the synthesis of HECs through reactive bipolar high-power impulse magnetron sputtering (HiPIMS) to overcome these conventional challenges.

Through HiPIMS, HEC crystals structurally and compositionally transform as a function of the carbon to metal ratio (C/M), providing access to metallic, ceramic, and composite carbides. By increasing the methane flow rate during sputtering, this introduces a carbon-deficient metallic ($C/M < 1$), transitions to a stoichiometric ceramic zone ($C/M \sim 1$), and finally culminate in an excess-carbon, nanocomposite regime ($C/M > 1$) at high methane flow rates. Combinations of X-ray diffraction, Raman spectroscopy, scanning electron microscopy, X-ray photoelectron spectroscopy, and nanoindentation/microindentation hardness measurements form these three zones. Achieving the stoichiometric ceramic zone is of particular interest to maximize the hardness of a given HEC composition. HiPIMS is able to produce HECs with ceramic zones over a larger range of methane flow rates than RF or DC sputtering.

9:20am **TF1+PS-FrM-4 Structural Evolution and Thermoelectric Properties of Flexible Mg_2Sn Films Prepared by Magnetron Co-sputtering***, **Sara Kim**, S. Kang, N. Kim,* Chosun University, Republic of Korea

Thermoelectric (TE) materials are capable of harvesting waste heat and converting it into useful electrical power which contributes significantly to improved energy efficiency. Recently, the development of flexible TE materials and devices has become a significant focus in the thermoelectric field due to the need for wearable and autonomous devices. The flexible TE materials can effectively harvest waste-heat from hot surfaces in a wide temperature range for applying to power generation in industry and human life. The anti-fluorite Mg_2X (X = Si, Ge, Sn)compounds have attracted great attention owing totheir non-toxicity, low manufacturing cost, light weight, and flexibility [1]. In this study, several un-doped Mg-Sn films were deposited onto polyimide substrates by radio frequency magnetron co-sputtering with Mg and Sn targets. Mg sputtering power was fixed while Sn sputtering power was varied to prepare Mg-Sn films with different stoichiometry. Then, Mg and Sn sputtering time was varied to prepare films with different thicknesses while the sputtering power was fixed. The TE performances as well as the flexibilityof the samples were analyzed in terms of point defects and structural evolution of the samples during flexibility test. Folding tests with different folding cycles were carried out for flexibility evaluation of the samples. The structural properties, chemical composition, and Hall characteristics of the Mg-Sn thin films before and after the folding test were analyzed using X-ray diffraction, energy dispersive X-ray spectroscopy, and Hall effect measurement system, respectively. The electrical resistivity and Seebeck coefficient as a function of temperature were simultaneously measured up to 703 K. Acknowledgement: This work was supported by the Gwangju·Jeonnam Local Energy Cluster Manpower Training of the Korea Institute of Energy Technology Evaluation and Planning (KETEP) grant funded by the Korea government Ministry of Trade, Industry and Energy (No. 20214000000560). [1] J. I. Tani, and H. Ishikawa, Thin Solid Films 692, 137601 (2019).

Thin Films Division
Room 316 - Session TF2+EM-FrM
Wide and Ultra-Wide Bandgap Thin Films: Advances in Deposition and Novel Materials

Moderators: Christophe Vallee, SUNY College of Nanoscale Science and Engineering, **Virginia Wheeler**, U.S. Naval Research Laboratory

10:00am **TF2+EM-FrM-6 AlGaN, An Enabling Ultra-Wide Bandgap Semiconductor***, **Dolar Khachariya**,* Adroit Materials*; M. Breckenridge, D. Szymanski, S. Stein,* North Carolina State University*; W. Mecouch,* Adroit Materials*; Y. Guan, P. Bagheri, S. Rathkanthiwar,* North Carolina State University*; P. Reddy, R. Kirste, S. Mita, B. Moody, J. Tweedie,* Adroit Materials*; K. Sierakowski, M. Boćkowski,* Institute of High-Pressure Physics, Poland*; E. Kohn, S. Pavlidis, R. Collazo, Z. Sitar,* North Carolina State University **INVITED**

III-nitride ultra-wide bandgap semiconductors offer a future alternative to maintain the growing demand for high-power devices. Current III-nitride devices already offer higher breakdown voltages (BV) and reduced on-resistances (R_{ON}) compared to Si and SiC. However, several power devices, such as junction barrier Schottky (JBS) diodes and superjunctions (SJ), which provide an improved BV and R_{ON} tradeoff, have not been demonstrated in III-nitrides. The major limitation is the difficulty of achieving selective area doping. In the JBS diode, p-regions must be laterally interspersed between n-regions below the anode contact. A SJ device requires alternating lateral n- and p-type doping regions with zero net charges. Two approaches can be considered to address this challenge: ion implantation and polarity control.

Currently, III-nitrides do not possess a robust ion implantation toolbox that allows for reliable implantation control and activation. Recent advances in ion implantation for the realization of n-type AlN and p-type GaN will be discussed. For n-type AlN, Si implantation was realized with the implementation of defect quasi-Fermi level control. The highest *n*-type conductivity in AlN will be demonstrated. For p-type GaN, we demonstrate the ability to successfully achieve *p*-type conductivity via Mg implantation and post-implantation annealing at ultra-high pressure. Using this technique, GaN JBS diode with low R_{ON} and high BV will be discussed.

The inherent polar doping selectivity of GaN can be used to achieve the doping scheme for a lateral GaN p/n junction. Oxygen, which unintentionally incorporates into N-polar GaN, acts as the n-type dopant, whereas Ga-polar GaN does not readily incorporate oxygen and remains undoped. Accordingly, lateral polarity junctions (LPJs) with alternating domains of O-doped N-polar and Mg-doped Ga-polar GaN have been fabricated to realize lateral p/n junctions. For drift regions, the n-type doping in the N-polar domain (and p-type doping in the Ga-polar domain) was reduced to ~10^{17} cm^{-3}. Implementing the chemical potential control (CPC) framework and supersaturation modulated growth (SMG), a GaN LPJ with a smooth surface and equal domain heights with the necessary doping profile will be discussed.

10:40am **TF2+EM-FrM-8 CVD of Crystalline and Amorphous sp^2-BN Thin Films on Different Orientations of Al_2O_3***, S. Sharma,* Linköping Univ., IFM, Thin Film Physics Div., Sweden*; **Laurent Souqui**,* University of Illinois at Urbana-Champaign*; H. Pedersen,* Linköping University, IFM, Sweden*; H. Högberg,* Linköping Univ., IFM, Thin Film Physics Div., Sweden

Thin films of epitaxially grown sp^2-hybridized boron nitride (sp^2-BN) in its hexagonal (h-BN) and rhombohedral (r-BN) phases have potential applications in optoelectronics and graphene technologies. Additionally, amorphous sp^2-BN (a-BN) is a promising material for electronic applications as a dielectric along with being a barrier for metal diffusion. Thin film growth of sp^2-BN is typically done using chemical vapor deposition (CVD). Growth of epitaxial sp^2-BN thin films requires high growth temperatures, above 1200 °C; for this reason, (0001) oriented sapphire (Al_2O_3) substrates are commonly used. Our study[1] investigates the growth of sp^2-BN using thermal CVD, comparing the differences in growth on Al_2O_3(11-20), Al_2O_3(1-102), Al_2O_3(10-10) and Al_2O_3 (0001), known as *a*-cut, *r*-cut, *m*-cut and *c*-cut substrates respectively, with an AlN buffer layer. For growth of sp^2-BN on these cuts, we use two boron precursors triethylborane (TEB) and trimethylborane (TMB), both along with NH_3 to investigate different chemical pathways.

Regardless of the boron precursor used, sp^2-BN growth on all the substrates was confirmed using Fourier transform infrared spectroscopy. X-ray Diffraction (XRD) $2\theta/\omega$ scans revealed that the sp^2-BN films grown on *c*-cut and *a*-cut were crystalline with the basal planes parallel to the substrate surface, while sp^2-BN films deposited on *r*-cut and *m*-cut were X-ray amorphous. XRD ϕ-scans showed the epitaxial growth of r-BN on *c*-cut and *a*-cut substrates. The in-plane relationship on the *a*-cut is r-BN[11-20]$\parallel$ w-AlN[11-20]$\parallel$ α-Al_2O_3[0001], which is similar to the *c*-cut. Using XRD ω-scan on the r-BN0003 peak, we determined that the crystal quality of r-BN is higher on the *a*-cut compared to the *c*-cut substrate; full width half maximum of 0.98° and 1.15° respectively. Scanning electron microscopy showed triangular shaped grains surrounded by less ordered material on the surface for the *c*-cut and *a*-cut while no such triangular features were seen on the *r*-cut and *m*-cut substrates. Our results show that epitaxial r-BN films are grown with determined in-plane orientations and with higher crystal quality on the *a*-cut. Conversely, a-BN films can be grown using the *r*-cut and *m*-cut substrates.

To advance the field, we will apply advanced analytical microscopy to study the differences locally, in terms of crystallinity, chemical bonding, and the influence of carbon in our deposited films. Additionally, other aspects of amorphous growth will be investigated.

(1) Sharma, S et al. Chemical Vapor Deposition of Sp^2 -Boron Nitride Films on Al_2O_3 (0001),(11-20),(1-102),and(10-10) substrates . *J. Vac. Sci. Technol. A***2022**,*40*(3),033404

11:00am **TF2+EM-FrM-9 Investigating SiC/Graphene/SiC(0001) Remote Epitaxy Using Hot-wall CVD***, **Daniel J. Pennachio,*** US Naval Research Laboratory*; J. Hajzus,* ASEE Postdoctoral Fellow at US Naval Research Laboratory*; A. Lang,* US Naval Research Laboratory*; R. Stroud,* Former employee of US Naval Research Laboratory*; R. Myers-Ward,* US Naval Research Laboratory

Remote epitaxy (RE) is a promising new technique for epitaxial film removal and substrate reuse that utilizes monolayer graphene as a release layer [1]. Graphene grown directly on SiC(0001) substrates through Si sublimation or through propane chemical vapor deposition (CVD) is an ideal platform for remote epitaxy of wide bandgap (WBG) semiconductors as there is no need for a graphene transfer step, reducing the risk of introducing contamination or defects that can complicate the study of the remote epitaxy process. In addition, this materials system is compatible with commercially-viable WBG semiconductor growth and processing. However, SiC CVD growth is typically conducted using high-temperature hydrogen-based chemistries that could damage or remove graphene. This study investigates the effect of alternate CVD growth conditions on SiC/graphene/SiC(0001) remote epitaxy and optimizes CVD parameters to produce high-quality SiC epilayers while reducing damage to the graphene barrier. In addition, since the effect of epitaxial graphene features such as SiC macrostep morphology and associated layer inhomogeneity on the RE process is currently unknown, graphene preparation and associated morphology is varied to explore its effect on SiC epilayer formation.

Semi-insulating nominally on-axis 6H-SiC(0001) and n-type 4° off-axis 4H-SiC(0001) substrates were used to produce different SiC surface morphologies and graphene layer numbers. $Ar:H_2$ process gas flow ratio, growth precursor C/Si ratio, and growth temperature were optimized during hot-wall CVD RE to promote smooth film morphology. Nomarski optical microscopy, scanning electron microscopy, and atomic force microscopy found CVD deposition at 1620°C with Ar/H_2 ratios <20/5 slm, and C/Si ratios <1.55 to have the smoothest surface morphology and fewest polytype inclusions. Substrates with offcuts <0.1° from SiC(0001) exhibited lower epilayer macrostep density, but showed evidence of polytype impurities and 3D growth at C/Si ratios > 1.0. Point defect density in RE SiC epilayers using a graphene interface was shown to be lower than SiC homoepitaxy using similar conditions without graphene. Cross-sectional transmission electron microscopy was utilized to assess the growth interface and graphene layer integrity after CVD growth. Through this study, optimal RE growth processes are suggested for a balance of graphene survivability and SiC film morphology.

[1] Kim, Y., Cruz, S., Lee, K. *et al. Nature* **544,** 340–343 (2017).

11:20am **TF2+EM-FrM-10 Sputter Deposition of III-N Thin Films***, **Joshua Nordlander,*** The Pennsylvania State University*; Z. Sitar,* North Carolina State University*; J. Maria,* The Pennsylvania State University

In this presentation, we demonstrate that reactive High-Power Impulse Magnetron Sputtering (HiPIMS) is an effective alternative for depositing high quality, epitaxial III-N thin films. In contrast to conventional direct current (DC) sputtering, HiPIMS provides the needed kinetic energy and ionization fraction to establish a sufficiently reactive environment to promote full nitridation.Specifically, the low duty cycle regime of HiPIMS provides access to kW/cm^2 peak power densities without target degradation and thus dramatically increased metal reactivity. In addition, adding an opposite polarity voltage pulse between the target bombarding events, known as a kick pulse, further allows one to tailor both the adatom landing energy on the substrate surface, and mitigate target poisoning.

This unique capability set enables us to prepare high crystal quality epitaxial InN thin films with low out-of-plane mosaicity and electron mobilities in excess of 400 cm^2/Vs with a step-and-terrace microstructure when deposited on AlN-nucleated sapphire substrates.Equilibrium supersaturation models are useful for predicting the surface microstructure of these films by varying the V/III ratio or deposition temperature.

In addition, homoepitaxial GaN thin films can be deposited at temperatures below 600°C with smooth surface morphologies characterized by c/2 steps and terraces.The presentation will focus on the relationships between sputtering parameters and III-N thin film crystal quality, surface morphology, and growth rate.

11:40am **TF2+EM-FrM-11 Thickness Dependent Properties of Ferroelectric Boron-Substituted Aluminum Nitride Thin Films***, **John Hayden**, J. Nordlander, W. Zhu, S. Trolier-McKinstry, J. Maria,* Pennsylvania State University

Recently discovered wurtzite structured ferroelectrics are interesting as next generation materials for ferroelectric memory devices, however they suffer from large leakage currents at small film thicknesses. In this work, we investigate the thickness dependent properties of ferroelectric boron-substituted aluminum nitride based thin films deposited by magnetron co-sputtering. Films grown on tungsten coated sapphire substrates show robust ferroelectricity for thicknesses as small as ~100 nm. Polarization hysteresis measurements of films thinner than 100 nm show inflated remanent polarization values from leakage currents. Electron microscopy studies and thickness dependent x-ray rocking curve measurements indicate there is a defect rich region near the film-electrode interface with reduced film crystallinity and out-of-plane mosaicity. In an attempt to improve film quality near the interface, films are grown on a variety of electrode materials with varying chemical and structural similarities to wurtzite structured aluminum nitride. Tungsten nitride is chosen as it is nitrogen containing, yet structurally dissimilar to aluminum nitride, while indium nitride is chosen because it is isostructural to aluminum nitride. For films grown on tungsten nitride, roughness and leakage currents decreased with decreasing electrode thickness, though no substantial improvements compared to films grown on W were observed. Films grown on epitaxial indium nitride/aluminum nitride/sapphire stacks adopt the stepped surface morphology of the InN and exhibit significantly narrower rocking curve widths compared with films grown on W. Film crystallinity, leakage current, and ferroelectric properties are investigated as a function of indium nitride surface morphology and ferroelectric film thickness.

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