Monday Morning, October 25, 2021

Live Session
Room Live - Session LI-MoM

AVS Plenary & Awards Session

Moderators: Timothy Gessert, Gessert Consulting, Dan Killelea, Loyola University Chicago, Amy Walker, University of Texas at Dallas

10:00am **LI-MoM-1 Welcome from the AVS President***, **Susan Burkett,*** University of Alabama

Welcome to the AVS 67 Virtual Symposium! We hope you will enjoy our Exciting Live and On Demand Sessions this week!

10:05am **LI-MoM-2 Welcome from the AVS 67 Program Chair***, **Dan Killelea,*** Loyola University Chicago

Welcome to the AVS 67 Virtual Symposium. I will review the structure of this week's program. We hope you will enjoy the event!

10:15am **LI-MoM-4 AVS Plenary Lecture: Pump-Probe Experiments with Neutral Matter: A New Approach to the Kinetics of Surface Reactions***, **Alec M. Wodtke,*** Georg-August University of Göttingen and The Max Planck Institute for Biophysical Chemistry, Germany **INVITED**

Knowledge of the rates of elementary gas phase reactions has contributed decisively to our understanding of important societal problems, for example stratospheric ozone chemistry. Growing our knowledge of rates of elementary chemical reactions at surfaces is crucially important to improving heterogeneous catalysis. In comparison to gas phase reactions, there are surprisingly few known activation energies of elementary surface reactions, nor knowledge of the energies and entropies of the reactions' transition states. This situation is a result of limitations on our methods for measuring rate constants of elementary surface reactions. Furthermore, first principles theories to predict surface reaction rates remain largely un-validated. In this talk, I will present recent experimental advances yielding the rates of elementary reactions at surfaces, which rely on a stroboscopic pump-probe concept designed for neutral matter. This method is also capable of revealing surface-site-specific kinetics information. Not only is site specific reactivity an essential aspect of surface reaction mechanisms, it is essential to provide benchmarks for testing first principles methods for calculating reaction rates, another potentially powerful tool with which to investigate heterogeneous catalysis.

11:00am **LI-MoM-13 2021 Dorothy M. and Earl S. Hoffman Award Scholarship Talk: Formation and Stability of Oxygen Structures on Ag(111) Surfaces***, **Marie Turano**[1],* Loyola University Chicago*; L. Juurlink,* Leiden University, The Netherlands*; E. Jamka, M. Gillum, D. Killelea,* Loyola University Chicago

We have studied oxidized Ag(111) surfaces after exposure to gas-phase O atoms using a combination of surface science techniques to determine the resultant surface structure. The total oxygen incorporation was determined with temperature programmed desorption (TPD) and the surface structures were determined with low energy electron diffraction (LEED) and scanning tunneling microscopy (STM). A long-standing challenge in the study of heterogeneously catalyzed oxidation reactions on silver surfaces is the determination of what surface species are of greatest chemical importance. This is due to the coexistence of several different oxygen reconstructions on oxidized silver surfaces. A further complication is subsurface oxygen (Osub) or O atoms dissolved into the near surface region of a metal, which alters the surface structure and reactivity of the metal. However, the effects of Osub have yet to be well characterized. Using a curved Ag(111) single crystal with two step types, we investigated the influence of terrace width and step geometry on oxidation and reconstruction formation on a well characterized Ag surface. Upon exposure of a curved Ag(111) crystal to gas-phase O atoms at 525 K, we observed a non-uniform oxygen accumulation over the crystal surface. Quantitatively, O desorption was identical to planar Ag(111) as verified by TPD. However, through STM images, we determined that A-type steps massively reconstruct with reconstruction forming at the bottom edge of steps and spreading outward. B-type steps exhibit a different growth mechanism where steps are originally pinned by initial oxidation and thus hinder the formation of reconstruction.

In addition, after oxygen exposures at low temperatures (T = 450 K) resulting in Osub formation, the surface showed the coexistence of a previously characterized stripe structure as well as an amorphous pattern. Annealing this exposure resulted in familiar surface reconstructions implying that the Osub changes the surface structure on curved Ag(111). Based on these findings, we demonstrate the complexity of the silver surface under oxidizing conditions and the importance of Osub in resultant surface structures.

11:15am **LI-MoM-16 AVS 2021 Graduate Research Award Talk: Molecular Interactions with Frozen Ice Films: Adsorption, Oxidative Reactivity, and Isotopic Enrichment***, **Michelle Brann**[2], S. Sibener,* University of Chicago

My research seeks to experimentally model surface-mediated processes occurring on icy-dust grains to develop a more complete understanding of the formation of planetary atmospheres, complex organic molecules, and origin of life in the universe. I use a state-of-the-art ultra-high vacuum (UHV) chamber that mimics the low-pressure conditions seen in astrophysical environments with optics for *in-situ* Reflection Absorption Infrared Spectroscopy (RAIRS). This chamber is connected to a molecular beam line that produces reactant gases with highly customizable energies for exposure onto the desired substrate. My goal is to understand how impinging molecules adsorb, react, or diffuse into frozen ice films as this is often a first step for reactions to occur resulting in new organic molecules essential for life. This talk is split into three sub-projects: (1) initial sticking probability of methane on ice films with varying porosities and crystalline structures, (2) oxidative reactivity of frozen propene films, and (3) differential condensation of methane isotopologues. For each study, changes on the surface were monitored in real time with RAIRS and mass spectrometry techniques.

I determined that more methane ended up sticking onto the porous amorphous water films, compared to the crystalline films suggesting that porous are more efficient at dissipating energy. Similarly, when examining propene oxidation, I also found that film structure was important for reactivity. In this case, I identified, through careful analysis of RAIR spectra, that I could form both an ordered as well as an amorphous propene film depending on the deposition temperature; yet, oxygen was only able to react with the ordered propene film. Lastly, I observed preferential increased sticking and condensation for CD_4 on a CH_4 film compared to CH_4, confirming an isotopic enrichment. These results suggest that there is more efficacious gas-surface energy transfer involving multiphoton excitations for the heavier isotopologue. Overall, these results are important to create accurate models of surface mediated astrophysical and terrestrial processes and understand formation of the universe.

11:30am **LI-MoM-19 2021 AVS Russell and Sigurd Varian Award Talk: Chemically Resolving Metal Supported Regioisomeric Assemblies at the Angstrom Scale using Ultrahigh Vacuum Tip-Enhanced Raman Spectroscopy: Conformations & Interactions***, **Sayantan Mahapatra**[3], J. Schultz, L. Li, N. Jiang,* University of Illinois at Chicago

Conventional spectroscopic techniques are limited by the optical diffraction limit to about half wavelength and therefore offers 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 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-H2F20TPPDL) by scanning tunneling microscopy (STM), ultrahigh vacuum (UHV) TERS on Ag(100) with the spatial resolution down to 8 Å, which has wide range of applications in various field of surface science & nanotechnology such as regioselective catalysis reaction, chemical reactions, molecular electronics etc. We have shown, 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. In addition, the molecule-substrate interactions have been addressed at the single-molecule level by employing three 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. Expanding upon this work, the chemical information available through STM-TERS allows me to track a complete chemical reaction, from reactant to product, with single chemical bond sensitivity. Angstrom scale chemical analysis using TERS is shown here as a broad and versatile technique in surface characterization.

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[1] **National Student Award Finalist**

[2] **National Student Award Finalist**

[3] **National Student Award Finalist**

11:45am **LI-MoM-22 2021 AVS Graduate Research Award Talk: Investigating Surfaces, Interfaces, and their Impact on Degradation of Polymer Electrolyte Membrane Water Electrolyzers*, Sarah F. Zaccarine*[1]*,*** Colorado School of Mines*; M. Shviro,* Forschungszentrum Jülich GmbH, Germany*; M. Dzara,* Colorado School of Mines*; M. Carmo,* Forschungszentrum Jülich GmbH, Germany*; S. Pylypenko,* Colorado School of Mines

Hydrogen is an attractive option for renewable energy applications due to its ability for large quantities to be stored over a long period of time, but current H_2 production from fossil fuels is a major CO_2 emitter; consequently, there is a need for efficient, renewable H_2 production.[1] Polymer electrolyte membrane water electrolysis (PEMWE) is a promising strategy, but major degradation issues and the slow kinetics of the anodic oxygen evolution reaction (OER) limit commercialization. Ir has been shown to be the most active metal towards the OER, while IrO_2 is typically more stable in the harsh oxidizing conditions of this reaction. Both materials face high costs and limited availability, motivating studies of PEM electrolyzers with low loadings.

Commercial Ir and IrO_2 black catalysts were obtained and studied as catalyst powders, fresh membrane electrode assemblies (MEAs), and tested MEAs following durability cycling at different conditions. A variety of surface and bulk characterization techniques were employed to evaluate changes in the catalyst morphology and composition, electrode composition and structure, and various interfaces that exist in this system in order to understand their respective contributions towards degradation. Information about catalyst composition was obtained with surface-sensitive x-ray photoelectron spectroscopy (XPS) and bulk x-ray absorption spectroscopy (XAS). Scanning electron microscopy (SEM) and scanning transmission electron microscopy (STEM) combined with energy-dispersive x-ray spectroscopy (EDS) mapping of the electrode cross-sections were used to elucidate morphological and structural information as well as elemental distribution as a function of various durability conditions. Further, transmission x-ray microscopy (TXM) was used to visualize electrode structure at a larger scale than possible with electron microscopy methods. Results demonstrate that a systematic, multi-scale, multi-technique characterization approach is necessary to isolate contributions of the catalyst, ionomer, and overall CL morphology, composition, and structure on degradation of the PEM electrolyzer. These findings advance fundamental understanding towards development of more efficient electrodes, highlighting the importance of optimizing uniformity of the electrodes.

(1) Ayers, K. E. The Potential of Proton Exchange Membrane–Based Electrolysis Technology. *Curr. Opin. Electrochem.***2019**, *18*, 9–15.

(2) Spöri, C.; Kwan, J. T. H.; Bonakdarpour, A.; Wilkinson, D. P.; Strasser, P. *Angew. Chemie Int. Ed.***2017**, *56* (22), 5994–6021.

(3) Alia, S. M.; Stariha, S.; Borup, R. L. *J. Electrochem. Soc.***2019**, *166* (15), F1164–F1172.

12:15pm **LI-MoM-28 AVS 2021 Peter Mark Memorial Award Lecture: Novel MBE Approaches for Atomically Precise Synthesis of "Stubborn" Metal Oxides*, Bharat Jalan*[2]*,*** University of Minnesota, USA **INVITED**

Our ability to synthesize atomically-precise materials has continued to drive modern technology and fundamental study. Consider an element that is hard to oxidize and also difficult to evaporate, how do we create an atomically precise thin films of such metals, metal oxides or their heterostructures? This has been a key question in the synthesis science for many decades.

In this talk, I will present my group's effort to address this question. We have recently shown that both the low vapor pressure and difficulty in oxidizing a "stubborn" element can be addressed by using a *solid* metal-organic compound with significantly higher vapor pressure, and with the added benefits of being in a pre-oxidized oxidation state along with excellent thermal and air stability. Using this approach, we show, for the first time, the synthesis of Pt, RuO_2 and $SrRuO_3$ films with the *same ease and control* as afforded by III-V MBE. I will present a detailed MBE growth study combined with structural and transport characterizations. The effect of film thickness, orientation, strain, and defects such as cation vacancies on electronic properties will be discussed. In second part of my talk, I will present our work on the development of radical-based MBE approach for wide band gap alkaline stannates ($BaSnO_3$ and $SrSnO_3$) growth combined with their detailed structure and transport study.

12:45pm **LI-MoM-34 2021 AVS Nellie Yeoh Whetten Award Talk:Efficient Near-Infrared Emission from Lead-Free Ytterbium-Doped Cesium Bismuth Halide Perovskite Thin Films*, Minh Tran*[3]*,*** *I. Cleveland, G. Pustorino, E. Aydil,* New York University

All-inorganic metal halide perovskites have attracted significant attention for applications as solar cells, light-emitting diodes, and photodetectors because they have strong and tunable absorptions and emissions. Lead-based perovskites have been the focus of many studies because they perform well in these applications, but lead is toxic. Bismuth-based halide perovskites are non-toxic alternatives to widely researched lead-containing halide perovskites for optoelectronics. Cesium bismuth bromide, in particular, may have suitable optical properties, but optical absorption and photoluminescence (PL) data reported to date are contradictory. We resolved these literature discrepancies and showed that $Cs_3Bi_2Br_9$ thin films deposited by physical vapor deposition (PVD) via coevaporation of CsBr and $BiBr_3$ show absorption and emission peaks at 433 and 472 nm, respectively. Peak location and lineshapes of blue-shifted absorption and emission previously reported and attributed to quantum confinement in $Cs_3Bi_2Br_9$ nanocrystals could be reproduced in $BiBr_3$ solutions in different solvents even without any $Cs_3Bi_2Br_{9-}$. This suggests that high photoluminescence quantum yield (PLQY) and blue-shifted emissions reported below 472 nm may be originating from unreacted precursors and impurities in nanocrystal dispersions rather than from $Cs_3Bi_2Br_9$. We also doped $Cs_3Bi_2Br_{9-}$ films with Yb to investigate the possibility of quantum cutting, generation of *two* near-infrared (NIR) photons (1.25 eV) from each ultraviolet or blue photon absorbed at energies >2.5 eV. Coating silicon solar cells with a material that can achieve quantum cutting with PLQY approaching 200% (2 photons for every high energy photon) has the potential to increase the silicon solar cell efficiencies above the Queisser limit, 33%. The addition of Yb that can substitute up to 50% of the Bi in $Cs_3Bi_2Br_9$ leaves the $Cs_3Bi_2Br_9$ structure unchanged and results in NIR $Yb^{3+2}F_{5/2} \rightarrow {}^2F_{7/2}$ emission (1.25 eV) with 14.5% quantum yield. A PLQY of 14.5% from Yb-doped $Cs_3Bi_2Br_9$ is promising because undoped $Cs_3Bi_2Br_9$ is otherwise not emissive due to rapid nonradiative recombination: the highest reliably measured visible PLQY in the literature is only 0.2%. Despite this, energy transfer from $Cs_3Bi_2Br_9$ to Yb appears to compete efficiently with nonradiative recombination and results in a 14.5% quantum yield. Moreover, NIR emission decreases sharply when the perovskite host's bandgap is reduced below 2.5 eV, twice the Yb^{3+} emission energy, by substituting bromine with iodine, raising the possibility that the emission mechanism may involve quantum cutting. This also raises the tantalizing possibility that $Cs_3Bi_2Br_9$ could be a potential lead-free quantum cutting material for solar spectrum shaping to increase solar cell efficiency.

1:00pm **LI-MoM-37 AVS 2021 John Thornton Memorial Award Lecture: Oxide MBE Rocks! Reflections on 35$^+$ Years of *Oxide* MBE*, Darrell Schlom*[4]*,*** Cornell University **INVITED**

Molecular-beam epitaxy (MBE) is the "gold standard" synthesis technique for preparing semiconductor heterostructures with high purity, high mobility, and exquisite control of layer thickness at the atomic-layer level. Its use for the growth of multicomponent oxides got off to a rocky start 36 years ago, but in the ensuing decades, it has become the definitive method for the preparation of oxide heterostructures too, particularly when it is desired to access metastable polymorphs of oxides and the novel properties they possess. In this talk I will highlight a few examples from our* work over the past >30 years demonstrating how the atomic-layer control made possible by oxide MBE can be used to break synthesis rules and create metastable compounds and heterostructures with intreguing properties. Many important growth tricks, first developed for the growth of compound semiconductors by MBE, are equally applicable to the growth of oxides. Examples include the use of strain engineering, interface engineering, epitaxial stabilization, or dimensional confinement. These can be used to transmute oxides that are usually "vegetables" into metastable polymorphs that are ferroelectric, ferromagnetic, both at the same time (multiferroic), or superconducting. A key element of this modern alchemy is the availability of substrates with appropriate structural motifs to strain these complex oxide thin films by several percent—far beyond where they would crack or plastically deform in bulk—or to stabilize metastable polymorphs. I will also discuss some of the technical challenges to the controlled synthesis of oxides in thin film form that have been overcome. The ability of MBE to customize oxide structures with atomic-level control and impart controlled strain have made oxide MBE the technique of choice

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[1] **National Student Award Finalist**

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

[3] **National Student Award Finalist**

[4] **John A. Thornton Memorial Award Winner**

for precisely preparing epitaxial oxide heterostructures to understand and exploit their novel properties.

*The work reported was performed in collaboration with superb students, postdocs, colleagues, and collaborators from around the world. Although it is only possible to acknowledge a small fraction, I celebrate the achievements being honored by this award with the pioneering contributions of Jim Eckstein and Ivan Bozovic—with whom I began this journey and continue to work—together with the contributions and advice from leading collaborators: Long-Qing Chen, Chang-Beom Eom, Craig J. Fennie, Venkat Gopalan, Stanislav Kamba, Lena F. Kourkoutis, Jeremy Levy, Jochen Mannhart, David A. Muller, Nate Orloff, Xiaoqing Pan, Karin M. Rabe, Ramamoorthy Ramesh, Kyle M. Shen, Dmitri A. Tenne, Susan Trolier-McKinstry, Nicola A. Spaldin, Reinhart Uecker, and Xiaoxing Xi.

1:45pm **LI-MoM-46 2021 AVS Graduate Research Award Talk: Versatile Polymer Nanoparticle Synthesis Using Initiated Chemical Vapor Deposition (iCVD)**, ***Trevor Donadt***[1]*, D. Streever, R. Yang,* Cornell University

Polymerization of monomers to form nanoparticles (i.e. bottom-up synthesis) is commonly performed in liquid environments which confers restrictions to monomer chemistries and particle shape based on solubility and procedures that are commonly driven by surface tension. Here we report the synthesis of polymer nanoparticles (PNPs) through a technique performed in a chemical vapor deposition apparatus that traditionally forms thin film polymer coatings. By utilizing an initiated chemical vapor deposition (iCVD) reactor, the synthesis process is afforded the advantages of an all-dry process, enabling PNPs made of insoluble polymers (e.g., hydrophobic and heavily cross-linked) and a variety of chemistries (zwitterionic, fluorinated, functionalizable, etc.) using the same technique. Furthermore, the solvent-free process enables control of the PNP diameters across an impressively broad range, from below 10 nm to above 1 µm. This approach delivers unprecedented synthetic capability for PNPs with nanoscale control over particle size without relying on laborious nanofabrication of templates, which are commonly required for particle size control in existing procedures. The approach is also substrate-independent, such that it can be performed on any type of material, turning PNPs into nanostructured thin films in situ. This technique is compatible with a library of over 70 functional monomers developed to date for iCVD. The chemical versatility, combined with the broad yet precise control of particle sizes, renders this approach a promising route to generating PNPs from materials inaccessible in liquid-based methods, thus opening new avenues for PNP applications.

2:00pm **LI-MoM-49 2021 Dorothy M. and Earl S. Hoffman Award Scholarship Talk: Tunable Photonics Based on Thin-Film Vanadium Dioxide**, ***Chenghao Wan***[2], University of Wisconsin - Madison*; Z. Zhang,* Purdue University*; D. Woolf,* Physical Sciences Inc.*; J. Rensberg, M. Hafermann,* Friedrich Schiller University Jena, Germany*; J. Salman, Y. Xiao,* University of Wisconsin - Madison*; M. Park,* Purdue University*; C. Ronning,* Friedrich Schiller University Jena, Germany*; S. Ramanathan,* Purdue University*; M. Kats,* University of Wisconsin - Madison

Vanadium dioxide (VO_2) is a prototype strongly correlated material that undergoes a first-order insulator-to-metal transition (IMT) at ~70 °C. This reversible IMT in VO_2 has drawn decades-long research attention because it can result in orders-of-magnitude changes in carrier density accompanied by a dramatic change in the refractive index, which has advanced various applications in electronics and optics. Recently, improvements in deposition techniques have enabled synthesis of high-quality VO_2 thin films (with thickness of tens of nanometers), boosting the utilization of thin-film VO_2 in nanophotonics.

In this talk, we will first present our characterization and analysis of optical properties of thin-film VO_2 for wavelengths from the ultraviolet to the far infrared. Both ellipsometry data and effective-medium modeling will be presented, for VO_2 films grown using different methods, on different substrates, and with different thicknesses. Based on ellipsometry measurements, we have concluded that VO_2 films synthesized via different conditions generally feature consistent and large refractive-index contrast in the mid-infrared, but distinguishable (or even significantly different) optical properties in the visible and far infrared. Our data is freely available for anyone to use in their own design and simulations.

In the second part of the talk, we will give specific illustrations of tunable photonic devices by incorporating thin-film VO_2 into two kinds of nanophotonic geometries—metasurfaces and thin-film assemblies. For the metasurface-based design, we demonstrated an ultrathin reflective optical limiter comprising a $VO\text{-}_2$ thin film and metallic aperture antennas. Our design can feature intensity-dependent modulation of transmission for a broad wavelength range (>2 µm at 10 µm) and angle of incidence (up to 50° away from the normal, for all polarizations). For the thin-film design, we demonstrated a tunable broad-to-narrow bandpass filter by introducing a VO_2 film into a dielectric stack of alternating Ge and ZnSe layers. The fabricated filter can switch between a broadband transmission window in the long-wave infrared (8 – 12 µm) and a narrow passband centered around 8.8 µm, which has potential uses for thermal-imaging enhancement.

In the end, we will also briefly discuss our engineering of the IMT temperature in VO_2 films by defect engineering via ion implantation, which can enable applications close to room temperature.

2:15pm **LI-MoM-52 2021 AVS Dorothy M. and Earl S. Hoffman Award Talk: Strain Engineering of Magnetism and Topological States in Rippled Heusler Membranes**, ***Dongxue Du***[3]*, S. Manzo, C. Zhang, V. Saraswat,* University of Wisconsin - Madison*; K. Genser, K. Rabe,* Rutgers, The State University of New Jersey*; P. Voyles, M. Arnold, J. Kawasaki,* University of Wisconsin - Madison

Single-Crystalline Membranes of Functional Materials Enable the Tuning of Properties via Extreme Strain States; However, Conventional Routes for Producing Membranes Require the Use of Sacrificial Layers and Chemical Etchants, Which Can Both Damage the Membrane and Limit the Ability to Make Them Ultrathin. Here We Demonstrate the Epitaxial Growth of the Cubic Heusler Compound Gdptsb on Graphene-Terminated Al_2O_3 Substrate. Despite the Presence of the Graphene Interlayer, the Heusler Films Have Epitaxial Registry to the Underlying Sapphire, as Revealed by X-Ray Diffraction, Reflection High Energy Electron Diffraction, and Transmission Electron Microscopy. The Weak Van Der Waals Interactions of Graphene Enable Mechanical Exfoliation to Yield Free-Standing Gdptsb Membranes, Which Form Ripples When Transferred to a Flexible Polymer Handle. Whereas Unstrained Gdptsb Is Antiferromagnetic, Measurements on Rippled Membranes Show a Spontaneous Magnetic Moment at Room Temperature, With a Saturation Magnetization of 5.2 Bohr Magneton Per Gd. First-Principles Calculations Show That the Coupling to Homogeneous Strain Is Too Small to Induce Ferromagnetism, Suggesting a Dominant Role for Strain Gradients. We Will Also Describe Preliminary Magnetotransport Measurements Aimed at Tuning the Topological Properties of Gdptsb, Since This Compound Shares a Similar Electronic Structure as the Weyl Semimetal Gdptbi. Together, Our Results Point to Strained Membranes as a Powerful Platform for Tuning Magnetism and Topological States in Quantum Materials.

2:30pm **LI-MoM-55 AVS 2021 Medard W. Welch Award Lecture: Probing and Controlling Excitons in 2D Semiconductors**, ***Tony Heinz***[4]*,* Stanford University and SLAC National Accelerator Laboratory **INVITED**

One of the key features of the optical response of 2D semiconductors is the dominant role of excitonic interactions. The strong influence of these many-body effects reflects the reduced dimensionality combined with the reduced dielectric screening of atomically thin crystals. In this paper, we will review progress in understanding the nature of optically excited states in 2D monolayers and heterostructures. We will describe how excitonic states can be tuned and probed be altering the Coulomb interaction within the layer by various approaches, including through changes in the external dielectric environment. We will particularly emphasize recent advances in applying time-resolved ARPES (angularly resolved photoemission spectroscopy) to examine the momentum-space character and dynamics of excitons in transition metal dichalcogenide semiconductors. In these studies, carried out in collaboration with the group of Keshav Dani, we have been able not only to determine the valley characteristics of both bright and dark excitons, but also to image directly the wavefunction of excitonic states in momentum space. Examples of this approach will be presented both for monolayers and for vertical heterostructures.

3:00pm **LI-MoM-61 Closing Remarks and Thank You's**, ***Amy V. Walker***, University of Texas at Dallas

Thank you for attending the AVS 67 Plenary and Awards Session. We look forward to seeing you tomorrow at 10:00 am EDT for a full day of Live Parallel Sessions. Remember to check out the AVS 67 On Demand Sessions which are now available in the mobile app and online scheduler.

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[1] **National Student Award Finalist**

[2] **National Student Award Finalist**

[3] **National Student Award Finalist**

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

Live Session

Room Live - Session LI-TuM1

Tuesday Morning Live Session I: New Frontiers in Interfaces

Moderators: Ashleigh Baber, James Madison University, Erin Iski, U. Tulsa

10:00am **LI-TuM1-1 Welcome and Opening Remarks***, **Ashleigh Baber**,* James Madison University

Welcome to the AVS 67 Virtual Symposium! We hope you will enjoy the event!

10:05am **LI-TuM1-2 Electrochemical Surface Science of Platinum***, **Marc Koper**,* Leiden University, Netherlands **INVITED**

Platinum is the most used electrocatalyst in electrochemical energy conversion devices such as fuel cells and electrolysers. In this talk I will highlight the recent work of my group on understanding the surface chemistry of platinum in an aqueous electrolyte, by combining single-crystal electrochemistry, density functional theory calculations, ultra-high-vacuum modeling, in situ spectroscopy and in situ electrochemical scanning tunneling microscopy. I will challenge some existing explanations and interpretations of platinum electrochemistry, and show the sometimes surprising surface disordering of platinum that happens at both positive (anodic) and negative (cathodic) potentials.

10:25am **LI-TuM1-6 Manipulating Electrochemical Reactions in Van Der Waals Heterostructures***, **Kwabena Bediako**,* University of California at Berkeley **INVITED**

Molecular-scale manipulation of electronic and ionic charge accumulation in materials is the backbone of electrochemical energy storage. Layered van der Waals (vdW) crystals are a diverse family of materials into which mobile ions can electrochemically intercalate into the interlamellar gaps of the host atomic lattice. The structural diversity of such materials enables the interfacial properties of composites to be optimized to improve ion intercalation for energy storage and electronic devices. However, the ability of heterolayers to modify intercalation reactions, and their role at the atomic level, are yet to be elucidated. In this talk I will discuss the electrointercalation of lithium at the level of individual atomic interfaces of dissimilar vdW layers. In this work, electrochemical devices based on vdW heterostructuresof stacked hexagonal boron nitride, graphene and molybdenum dichalcogenide (MoCh_2; Ch= S, Se) layers were constructed. Transmission electron microscopy, in situ magnetoresistance and optical spectroscopy techniques, as well as low-temperature quantum magneto-oscillation measurements and ab initio calculations, were used to resolve the intermediate stages of lithium intercalation at heterointerfaces. The formation of vdW heterointerfaces between graphene and MoCh_2 layers was found to result in a more than tenfold greater accumulation of charge in the metal dichalcogenidewhen compared to MoCh_2/MoCh_2homointerfaces, while enforcing a more negative intercalation potential than that of bulk Mo$Ch_2$by at least 0.5 V. Beyond energy storage, this combined experimental and computational methodology for manipulating and characterizing the electrochemical behavior of layered systems opens new pathways to control the charge density in two-dimensional electronic and optoelectronic devices.

10:45am **LI-TuM1-10 Scale-Up Manufacturing Processes for Powders: Pairing Powder Properties to Process***, **Arrelaine Dameron**, S. Moulton, J. DuMont , D. Lewis, T. Porcelli, R. Tracy,* Forge Nano **INVITED**

Control of surface phenomena by powder modification via atomic layer deposition (ALD) for a spectrum of technology applications has made its way to R&D literature. But commercial adoption of ALD powder modification has been perceived as slow and too expensive to consider as a realistic commercial process. Forge Nano has patented, constructed, and demonstrated a high throughput ALD powder manufacturing capability at commercial scale and is commercializing first markets with partners. The manufacturing capability for powder modification with ALD is unlocking new potential for lower-cost integration of ALD into products. We will discuss a cross-comparison of ALD manufacturing type to product application and scaling requirements. For the first time in history, a pathway for ALD-enhanced materials to be rapidly transitioned from lab-scale demonstration to commercial presentation is available for new product development. The scaleup process addresses the stepwise progression to validate engineering and materials requirements to meet the market price demands. We will demonstrate that ALD enabled materials are the state of the art. The manufacturing of consistent materials with ALD modification is a cost-competitive level and now possible. The future of material science and product development for operation at more demanding conditions is enabled by ALD for a variety of applications.

11:15am **LI-TuM1-16 Batteries at Work: Ambient Pressure Photoelectron Spectroscopy for Lithium Ion Batteries***, I. Källquist, F. Lindgren, M. Hahlin,* Uppsala University, Angstrom Laboratory, Sweden*; **Julia Maibach**,* Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM), Germany **INVITED**

Rechargeable ion batteries such as Li-ion batteries generally consist of a negative electrode, a positive electrode and an ion conducting electrolyte. Today, much of our knowledge about the interactions of these components at surfaces and interfaces comes from post mortem photoelectron spectroscopy (PES) analyses. For these types of measurements, pre-cycled battery electrodes are transferred to the PES instrument to be characterized in UHV conditions.

Using ambient pressure photoelectron spectroscopy (APPES), we now have the possibility to acquire more realistic information about the interplay of electrode and electrolyte since the experiments can be conducted at elevated pressures and with liquid electrolyte present. We will firstly present our contributions to characterizing Li-ion battery electrodes [1] and electrolytes [2] using APPES as a precondition to achieve reliable in-situ and operando studies on working batteries.

Secondly, we present our work on electrode/electrolyte interfaces to investigate changes in Galvani potential using *operando* APPES [3]. For Li-ion batteries, Galvani potential differences (i.e. the electrostatic potential difference between two phases in contact) play an important role for the reaction kinetics at the functional electrode/electrolyte interphases. However, due to lack of suitable measurement techniques, so far little is known about how the Galvani potential difference behaves during Li-ion battery operation. We will show our approach on measuring how a change in Galvani potential difference can be followed as a function of applied external voltage using *operando* APPES, even without direct access to the electrode/electrolyte interface.

[1] J. Maibach, C. Xu, S. K. Eriksson, J. Åhlund, T. Gustafsson, H. Siegbahn. H. Rensmo, K. Edström, M. Hahlin, Rev. Sci. Inst. 86 (2015), 044101.

[2] J. Maibach, I. Källquist, M. Andersson, S. Urpelainen, K. Edström, H. Rensmo, H. Siegbahn, M. Hahlin, Nature Comm. 10 (2019), 3080.

[3] F. Lindgren, I. Källquist, M.-T. Lee, A. Shavorskiy, K. Edström, H. Rensmo, L. Nyholm, J. Maibach, M. Hahlin, in preparation.

11:35am **LI-TuM1-20 In-Situ TEM Imaging of Nanoscale Reactions at Solid-Liquid-Gas Interfaces***, **Haimei Zheng**,* Lawrence Berkeley National Lab **INVITED**

Many chemical reactions involve the presence of solids, liquids and gases concurrently, for instance, heterogeneous catalysis, materials corrosion and others. Complex phenomena may occur at solid-liquid-gas interfaces. Direct monitoring the interfacial reactions at the nanoscale is significant for understanding the reaction mechanisms and developing strategies to control the reactions. By developing and applying liquid cell transmission electron microscopy (TEM), my group studies the dynamic nanoscale phenomena at solid-liquid-gas interfaces with high spatial and temporal resolution. In this talk, I will first show the observed accelerated etching of Au nanostructures with the presence of gas nanobubbles. Through tracking the evolution of local reaction profile and theoretical modeling, an understanding of the triple phase reactions and gas diffusion pathways at the interfaces is developed. I will also show that the solid-liquid-gas interfaces can play a critical role in mediating the oxidative etching by allowing the reduction reactions in a near distance. Future work on in situ TEM studies of the solid-liquid-gas interfaces and device applications will also be discussed.

11:55am **LI-TuM1-24 Molecular Processes in Ultra-High Vacuum between the Stars***, **Ewine van Dishoeck**,* Leiden University, The Netherlands **INVITED**

Stars and planets are born in the cold and ultra-tenuous clouds between the stars in the Milky Way. In spite of the extremely low temperatures and densities, a surprisingly rich and interesting chemistry occurs in these interstellar clouds, as evidenced by the detection of more than 200 different molecules. Water and a large variety of organic molecules are found, including simple sugars and high abundances of deuterated species. What are the molecular processes by which these molecules are formed and destroyed, both in the gas phase and on surfaces? And how do we calculate or measurerates that can be used in models of star-forming regions? Can these pre-biotic molecules end up on new planets and form the basis for life elsewhere in the universe? New data from the revolutionary Atacama Large Millimeter Array (ALMA) and the ESA-Rosetta mission to comet 67P will be presented.

12:15pm **LI-TuM1-28 Closing Remarks and Thank You's*, Erin Iski,*** University of Tulsa

Thank you for attending today's session! Please note that our afternoon sessions begin at 12:50 pm EDT. We also look forward to seeing you tomorrow at 10:00 am EDT for a full day of Live Parallel Sessions. Remember to check out the AVS 67 On Demand Sessions which are available in the mobile app and online scheduler.

Live Session
Room Live-2 - Session LI-TuM2

Tuesday Morning Live Session II: Current and Emerging Devices

Moderators: Adriana Creatore, Eindhoven University of Technology, Netherlands, Sebastian Engelmann, IBM T.J. Watson Research Center

10:00am **LI-TuM2-1 Welcome and Opening Remarks*, Adriana Creatore,*** Eindhoven University of Technology, The Netherlands

Welcome to the AVS 67 Virtual Symposium! We hope you will enjoy the event!

10:05am **LI-TuM2-2 Aluminum Scandium Nitride Microdevices for Next Generation Nonvolatile Memory and Microelectromechanical Systems*, Troy Olsson,*** University of Pennsylvania **INVITED**

Aluminum Nitride (AlN) is a well-established thin film piezoelectric material. AlN bulk acoustic wave (BAW) radio frequency (RF) filters were one of the key innovations that enabled the 3G and 4G smart phone revolution. Recently, the substitutional doping of scandium (Sc) for aluminum (Al) to form aluminum scandium nitride (AlScN) has been studied to significantly enhance the piezoelectric properties and to introduce ferroelectric properties into AlN based material systems. The properties achieved have profound implications for the performance of future 5G and 6G RF filters, piezoelectric sensors, piezoelectric energy harvesters, and for scaling the bit density of ferroelectric nonvolatile memories. This talk will present on the synthesis of highly Sc doped AlScN materials of the thickness and quality needed for applications in memory and microelectromechanical systems (MEMS). The material properties achieved will be reported and placed in the context of device specific figures-of-merit and competing material systems. Ferroelectric and electromechanical devices that utilize the unique properties of AlScN to achieve state-of-the-art (SOA) performance will be shown.

10:25am **LI-TuM2-6 Memristive Devices and Arrays as AI Hardware*, J. Joshua Yang,*** University of Southern California **INVITED**

Memristive devices have become a promising candidate as the AI hardware core due to their attractive properties(*1*). AI algorithms can be implemented on a Resistive Neural Network (ResNN) with memristor synapses and neurons or a Capacitive Neural Network (CapNN) with memcapacitor synapses and neurons(*2*).

For ResNNs as computing accelerators, we have built a dot-product engine based on a 128 x 64 1T1R crossbar array(*3*)and a 3D crossbar array with 8 layers of memristors(*4*)using traditional non-volatile memristors. With such computation accelerators, we have demonstrated efficient inference and learning with traditional Machine Learning algorithms(*5-7*), which is expected to significantly improve the speed and energy efficiency of neural networks.

For ResNNs beyond accelerator applications, we developed diffusive memristors(*8*)with diffusion dynamics that is critical for neuromorphic functions. Based on the diffusive memristors, we have further developed artificial synapses(*8*)and neurons(*9*)to more faithfully emulate their bio-counterparts. We then integrated these artificial synapses and neurons into a small neural network, with which pattern classification and unsupervised learning have been demonstrated(*9*).

For CapNNs, we have developed pseudo-memcapacitive devices based on the diffusive memristors. Capacitive synapses and neurons enabled by these memcapacitive devices have been developed and used to form a fully integrated CapNN(*10*), which can implement spiking signal classification and Hebbian-like learning.

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10:45am **LI-TuM2-10 Etch Processes for Enabling Next Generation Devices*, Eric Miller,*** *I. Seshadri, T. Kang, D. Metzler, J. Lee, S. Sieg, S. Engelmann, J. Shearer, J. Arnold, N. Felix,* IBM Research Division, Albany, NY **INVITED**

While delivering industry first demonstrations of 7NM (FinFET) and 5NM (Nanosheet) technology nodes, IBM Research has encountered unique challenges that arise as a result of continued device scaling. Dimensional compression drives higher aspect ratios, which in turn drive difficulty with in-feature ion, radical, and volatile species transport during plasma etch. Dimensional scaling now approaches the single digit nanometer scale, and the need for solutions to unique problems exists now more than ever. In the world of plasma etch, which largely led the charge in dimensional scaling with anisotropic patterning, it is now critical to account for a variety of factors to deliver a successful etch process. Etch process development is truly a juggling act of selectivity, anisotropy, by-product control, sidewall profile, and throughput. The continuation of device scaling using extreme ultraviolet light lithography, self aligned double and quadruple patterning, as well as the introduction of three dimensional (nanosheet) devices has introduced a unique set of challenges to be addressed in the coming technology nodes. In this paper, a variety of etch applications, challenges, and innovations will be reviewed with respect to continued device scaling. The functional implementation of quasi-atomic layer etching, plasma etch modulation of line edge/width roughness, and etch selectivity/anisotropy challenges at high aspect ratios will all be explored with the viewpoint of how these impact future semiconductor nodes.

11:15am **LI-TuM2-16 On the Low Deposition Rate and Ionized Flux Fraction in High Power Impulse Magnetron Sputtering*, Jon Tomas Gudmundsson,*** *H. Hajihoseini,* University of Iceland*; N. Brenning,* KTH Royal Institute of Technology, Sweden*; M. Rudolph,* Leibniz Institute of Surface Engineering (IOM), Germany*; M. Raadu,* KTH Royal Institute of Technology, Sweden*; D. Lundin,* Linkoping University, Sweden **INVITED**

The deposition rate in high power impulse magnetron sputtering (HiPIMS) is often found to be somewhat lower than that obtained with dc magnetron sputtering (dcMS), generally in the range of 30 - 85 % of the dcMS rates, depending on target material when operating at the same average power [1]. Back-attraction of ions of the sputtered species to the cathode target is probably the main cause for the low deposition rate while some other mechanisms have also been suggested. This includes the nonlinear sputter yield effect, guiding effect of the magnetic field, the increased density of the deposited film, the effect of different ion species on the sputter yield and that the sputtered material are being transported radially outward in the vicinity of the cathode. Some approaches to increase the deposition rate are discussed. We discuss how the magnetic field strength |**B**| and geometry (degree of balancing) influences the deposition rate and ionized flux fraction F_{flux} in dcMS and HiPIMS operation both axially [2] and radially [3]. The measured quantities, the deposition rate and ionized flux fraction, are then related to the ionization probability α_t and the back attraction probability of the sputtered species β_t. We find a significant transport of the film forming material radially or parallel to the target surface for both sputter techniques. This radial deposition decreases with increasing axial distance from the target surface and it is always higher in dcMS than HiPIMS. There are a significantly higher number of ions traveling radially in the HiPIMS discharge. We find that the relative radial flux of the film forming material is greater in dcMS compared to HiPIMS for almost all cases investigated. It is therefore concluded that the commonly reported reduction of the (axial) deposition rate in HiPIMS compared to dcMS does not seem to be linked with an increase in sideways material transport in HiPIMS. We discuss the tradeoff between a high ionized flux fraction of the sputtered species and a high deposition rate referred to as the HiPIMS compromise [4]. [1] M. Samuelsson, D. Lundin, J. Jensen, M. A. Raadu, J. T. Gudmundsson, and U. Helmersson, Surf. Coat. Technol. 202, 591 (2010)[2] H. Hajihoseini, M. Čada, Z. Hubička, S. Ünaldi, M. A. Raadu, N. Brenning, J. T. Gudmundsson, and D. Lundin, Plasma 2, 201 (2019).[3] H. Hajihoseini, M. Čada, Z. Hubička, S. Ünaldi, M. A. Raadu, N. Brenning, J. T. Gudmundsson, and D. Lundin, J. Vac. Sci. Technol. A 38, 033009 (2020).[4] N. Brenning, A. Butler, H. Hajihoseini, and M. Rudolph, J. T. Gudmundsson, T. Minea, and Daniel Lundin, J. Vac. Sci. Technol. A 38, 033008 (2020).

11:35am **LI-TuM2-20 β-Ga_2O_3 Resonant Micro/Nanoelectromechanical Systems (M/NEMS)**, ***Xu-Qian Zheng**, P. Feng,* University of Florida **INVITED**

Beta gallium oxide (β-Ga_2O_3) is an emerging ultra-wide bandgap (UWBG) semiconductor (E_g=4.5-4.9 eV). The crystal is outstanding in sustaining high electrical field because of its UWBG, making it attractive for power electronics, high-voltage/power radio frequency (RF), and harsh-environment applications [1]. Based on its UWBG, β-Ga_2O_3 crystal has an absorption edge around 275 nm, thus the material is intrinsically suitable for solar-blind ultraviolet (SBUV, λ<280 nm) detection [2]. In addition, thanks to the capability of growth from liquid phase, bulk β-Ga_2O_3 crystals can be cost-effectively synthesized with exceptional crystal quality. Furthermore, β-Ga_2O_3 possesses excellent Young's modulus (E_Y=261 GPa) and speed of sound (c=6600 m/s), suitable for making mechanical devices. The outstanding ensemble of attributes in β-Ga_2O_3 enables new UWBG micro/nanoelectromechanical systems (M/NEMS) for future electromechanically coupled and tunable β-Ga_2O_3 electronic, optoelectronic, and physical sensing devices and systems.

Here we present an overview of the β-Ga_2O_3 mechanical properties characterization in nanomechanical device platforms and development of β-Ga_2O_3 resonant M/NEMS by describing the recent advances in engineering β-Ga_2O_3 nanostructures into functional devices and exploration of their device physics. We demonstrate a family of β-Ga_2O_3 NEMS resonators with resonance frequencies in high frequency and very high frequency (HF/VHF) bands and quality (Q) factors up to 1700 at room temperature. We extract Young's modulus of 245–261 GPa for thin film β-Ga_2O_3 in the nanomechanical resonator platform [3]. In additional to basic nanomechanical devices, we demonstrate real-time SBUV light detection using oscillators enabled by β-Ga_2O_3 resonant NEMS [4]. We demonstrate β-Ga_2O_3 vibrating channel transistors (VCTs) for electromechanical coupling of the β-Ga_2O_3 M/NEMS resonators and depict the future design and equivalent-circuit modeling of such devices for >GHz operations [5]. We investigate the operation of β-Ga_2O_3 nanomechanical resonators in high temperature environment (up to 350 °C) and study its resonance frequency response under different pressures from atmospheric pressure down to ~15 mTorr. Our study facilitates the development and integration of β-Ga_2O_3 resonant M/NEMS on-chip with β-Ga_2O_3 electronic circuits, supplementing the rapidly emerging β-Ga_2O_3 electronics and optoelectronics.

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11:55am **LI-TuM2-24 In-Depth Feasibility Study of Dual Damascene Extension: Patterning, Dielectric Etch and Metallization**, ***Xinghua Sun**,* TEL Technology Center, America, LLC; *Y. Mignot,* IBM Research Division, Albany, NY; *C. Cole, E. Liu,* TEL Technology Center, America, LLC; *J. Church,* IBM Research Division, Albany, NY; *D. Santos, A. Raley,* TEL Technology Center, America, LLC; *S. Sieg,* IBM Research Division, Albany, NY; *P. Biolsi,* TEL Technology Center, America, LLC **INVITED**

As logic metal pitch keeps scaling aggressively, back end of line (BEOL) interconnects continue to push the limits of materials properties and integrations. Current extreme ultraviolet (EUV) single exposure limitation (28P) requires a new robust patterning scheme based on EUV multipatterning and new metallization integrations will likely be required due to the lack of liner/barrier and copper scaling at such small critical dimensions [1, 2].Alternative subtractive metallization scheme are being studied for very advanced node where resistance/capacitance (R/C) simulations shows benefit [1].

A key integration choice to make is whether to extend Damascene dielectric etch or move to subtractive metal etch. For Damascene dielectric, the key challenges are mask pattern assembly and EPE control, low k dielectric line wiggling and damage post etch, and liner/barrier induced high resistance after metallization [3, 4]. Subtractive metal etch presents cost issues, alignment concerns and will likely be implemented solely in first metal level(s) which have the most aggressive pitch scaling targets [3]. In terms of mask assembly, multipatterning is required to form line with a 3 masks level forSADP / cut / block and a 2 color Via mask (DPSAV) to meet design rules [4].

In this report, we present an in-depth study of the feasibility of Dual Damascene extension based on 24nm metal pitch. EUV self-aligned double patterning (SADP) is demonstrated for line and space patterning. With a cut and block flow, it enables an e-testable trench module. We demonstrate double patterned self-aligned via (DPSAV) for via tests. Dielectric reactive ion etch (RIE), including quasi atomic layer etch (QALE) and reduced low k damage etch, is leveraged for the trench and via formation, respectively. Finally, metallization and chemical mechanical planarization (CMP) is successfully demonstrated. This in-depth demonstration provides an important insight into Dual Damascene extension feasibility for future critical metal levels.

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12:15pm **LI-TuM2-28 Closing Remarks and Thank You's**, ***Sebastian Engelmann**,* IBM T. J. Watson Research Center

Thank you for attending today's session! Please note that our afternoon sessions begin at 12:50 pm EDT. We also look forward to seeing you tomorrow at 10:00 am EDT for a full day of Live Parallel Sessions. Remember to check out the AVS 67 On Demand Sessions which are available in the mobile app and online scheduler.

Live Session
Room Live - Session LI-TuA1

Tuesday Afternoon Live Session I: Harnessing and Understanding Interfacial Chemistry

Moderators: Donna Chen, University of South Carolina, Zhenrong Zhang, Baylor University

12:50pm **LI-TuA1-1 Welcome and Opening Remarks***, **Donna Chen,*** University of South Carolina

Welcome to the AVS 67 Virtual Symposium. I will review the structure of this week's program. We hope you will enjoy the event!

12:55pm **LI-TuA1-2 High-Throughput Computational Screening of Diamond Like Semiconductors and Ordered Vacancy Compounds for Thermoelectrics***, J. Xu,* University of Illinois at Urbana-Champaign*; C. Porter, J. Adamczyk, E. Toberer,* Colorado School of Mines*; **Elif Ertekin,*** University of Illinois **INVITED**

Computation-driven search for thermoelectrics (TEs) has recently shown several successes, but a principal bottleneck appears to be that predicted materials often prove to be difficult to dope in the lab. Here we will present our recent computational and experimental efforts to tailor the defect chemistry and dopability of a set of ordered vacancy compounds that are of interest for their TE potential. Ordered vacancy compounds (OVCs) are a family of materials whose structure is closely related to diamond like semiconductors, but contain an ordered array of vacancies. Diamond like semiconductors and OVCs are typically observed to be p-type, but our TE materials descriptor suggests that they would be more effective as thermoelectrics if they could be doped n-type. Therefore, we screen through a chemically-diverse set of 54 OVCs to assess their TE potential and dopability. For the most promising candidates, using calculations of phase stability defect formation energies, we comprehensively establish the achievable range of carrier concentrations achievable. Using phase boundary mapping, experimental carrier concentrations are measured and compared to the predicted values, typically showing correspondence within a few orders of magnitude. For all compounds, we find that a delicate competition between a set of dominant, competing defects governs the achievable range of carrier concentrations. For instance in the II_2-IV-VI_4 OVC structural prototype, enhancing n-type dopability requires suppressing the IV_{II} antisite and promoting the formation of the group II vacancy. Using this observation as a design strategy, we identify candidates that may be more amenable to n-type doping. The results of this search are used to generate a chemically intuitive framework for predicting dopabilities in this family of materials without the need to carry out full-scale first-principles analysis.

1:15pm **LI-TuA1-6 Towards a Mechanistic Understanding of Next-Generation Particle Accelerator Materials Growth: Nb Hydride Growth and Suppression and Nb_3Sn Formation on (3×1)-O Nb(100)***, **Rachael G. Farber**, S. Willson, R. Veit,* University of Chicago*; N. Sitaraman,* Cornell University*; A. Hire, R. Hennig,* University of Florida*; T. Arias,* Cornell University*; S. Sibener,* University of Chicago **INVITED**

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. However, prohibitively expensive operating and infrastructure costs prevent the implementation of accelerator-based technologies across a variety of sectors. Nb_3Sn is a promising next-generation material for SRF cavities and can operate at ~ 4.2 K, significantly reducing operating costs of cryogenic infrastructure. To increase the efficiency and accessibility of accelerator-based technologies, SRF materials must be developed that can reliably produce intense particle beams above 4 K.

Nb surface composition and contaminant incorporation directly affect *Q*. Hydrogen incorporated during Nb cavity fabrication results in the formation of Nb hydrides, which lower *Q* at high fields and reduce cavity performance. Nitrogen infusion of Nb cavities mitigates hydride formation, but the growth and suppression mechanisms of Nb hydrides are not thoroughly understood. Utilizing low-temperature scanning tunneling microscopy (LT-STM), scanning tunneling spectroscopy (STS), and density functional theory (DFT) calculations, we have investigated the growth and suppression mechanisms of Nb nano-hydrides on (3×1)-O Nb(100). STM and STS results identified the structural and electronic evolution of undoped, hydrogen doped, and co-doped Nb(100) resulting from Nb nano-hydride growth and suppression. DFT calculations corroborate experimental data and identified unique near-surface phases stabilized by dopant incorporation. These results provide the first *in situ*, real-time nanoscale characterization of the effects of dopant incorporation on Nb nano-hydride growth and suppression, elucidating the interplay between nitrogen and hydrogen regarding Nb SRF materials performance.

The latter part of this presentation will focus on the interaction of Sn with Nb substrates leading to the formation of Nb-Sn alloys. Nb_3Sn films are grown *via* Sn vapor deposition on preexisting Nb cavities. Sn homogeneity, surface roughness, and alloy thickness must be well controlled for high *Q* film growth, but the Nb_3Sn growth mechanism resulting in optimal film formation is not well understood. In this work, we have visualized Sn adsorption and diffusion behavior on (3×1)-O Nb(100) at the nanometer scale. STM data revealed preferential adsorption of Sn along the (3×1)-O unit cell. Annealing the Sn/Nb(100) sample resulted in the formation of hexagonal and rectangular Sn adlayer structures for all Sn coverages studied. STS measurements of these adlayers demonstrated thickness-dependent electronic properties that are distinct from the underlying Nb substrate. Genetic algorithm calculations and DFT based descriptors aim to determine energetically preferred Sn binding sites on the (3×1)-O surface. 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

1:35pm **LI-TuA1-10 Phase Formation and Thermal Stability of Reactively and Non-Reactively Sputtered High-Entropy Metal-Sublattice Carbides***, **Alexander Kirnbauer,*** TU Wien, Institute of Materials Science and Technology, Austria*; P. Polcik,* Plansee Composite Materials GmbH, Germany*; P. Mayrhofer,* TU Wien, Institute of Materials Science and Technology, Austria **INVITED**

High-entropy alloys (HEAs) and high-entropy metal-sublattice ceramics (HESCs) have recently gained particular attraction in the field of materials research due to their promising properties, such as high hardness, high strength, and thermal stability. Within this work, we report on the phase formation and thermal stability of high entropy metal-sublattice carbides to provide a further insight to a more extensive understanding of the high-entropy effect, according to which, based on the Gibbs-free energy, such materials should be stabilised in the high-temperature regime. Therefore, (Hf,Ta,Ti,V,Zr)C coatings were reactively and non-reactively sputtered from a single powder-metallurgically produced composite target (either metallic or consisting of the respective binary carbides). Reactively sputtered coatings were synthesised using an C_2H_2 – Ar mixture with different $C_2H_2/(C_2H_2+Ar)$ ratios (f_{C2H2}). After deposition, the coatings were investigated in as-deposited state and after vacuum annealing between 800 and 1200°C. The structure and morphology, the chemical composition, the mechanical properties, and the thermal stability of the coatings were investigated by scanning electron microscopy, X-ray diffraction, and nanoindentation.

The non-reactively sputtered as well as reactively sputtered coatings with f_{C2H2}= 20 % show a single-phased face-centred cubic (fcc) structure. The hardness for the non-reactively sputtered HESCs is with ~41 GPa higher than that of the reactively sputtered one which exhibits a hardness of 35 GPa. This indicates that due to the use of C_2H_2 also regions of amorphous carbon form, which slightly weaken the coating already in the as-deposited state. After vacuum annealing up to 1200 °C the non-reactively sputtered coatings maintain a hardness of ~40 GPa indicating retarded softening mechanisms due to sluggish diffusion. This behaviour was also observed in previous studies on different material classes such as nitrides, borides, and oxides indicating a stabilisation due to the high-entropy metal sublattice.

2:05pm **LI-TuA1-16 Electronic Structure and Dynamics of Single Atom Catalysts***, **Nuria Lopez,*** ICIQ, Spain **INVITED**

Single atoms have shown different structural and catalytic properties with deep coupling between the oxide and metallic structures. This phenomenum, unraveled by theory might have a high impact in the understanding of the chemical properties of the materials and might affect our current understading for materials included those that are active in energy-conversion proceses.

2:25pm **LI-TuA1-20 Methanol Synthesis Pathways for the Selective Conversion of C-H bonds***, **Sanjaya Senanayake,*** Brookhaven National Laboratory **INVITED**

Methane remains a valuable yet underutilized resource, with great interest for the direct upgrade to valued products. Our recent studies indicate that, in spite of the high stability of methane, systems such as Ni-CeO2(111) and CeO2-Cu(111) can break C-H bonds even at room temperature, through careful manipulation of interfaces and metal-support interactions, using light oxidants (CO2, O2/H2O). the selective oxidation on the surface sites can lead to conversion steps that produce CH3OH and CO+H2. AP-XPS with the help of DFT has been essential to elucidate C-H activation and oxidation steps with high resolution C 1s and O 1s spectroscopies.

We have established a method for the direct conversion of methane to methanol building on these surface results yielding low methanol selectivity (~30%). Subsequently, and in remarkable contrast we have found that a CeO2/Cu2O/Cu(111) inverse system is able to activate methane at room temperature and then, with the help of water, performs a highly selective (70%) catalytic cycle, for the production of methanol. The interfacial interaction between CeOx-CuOx is crucial while the concentration of water has a strong effect on the selectivity towards the production of methanol.

We have used AP-XPS to track the sequence of pathways that initially activate C-H bonds into -OCH3 surface species that leads to the production of methanol. DFT and KMC were then used to evaluate the most prevalent steps that are likely essential for such selective chemistry.

This work is funded by the U.S. Department of Energy under contract No. DE-SC0012704. XPS measurements were performed at beamline 9.3.2 at the Advanced Light Source of LBNL under contract no. DE-AC02-05CH11231.

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2:45pm **LI-TuA1-24 Building Bridges Between University, National Laboratory, and Industrial Research*, Robert McCabe,*** National Science Foundation **INVITED**

From the earliest days of UHV single-crystal and thin-film research related to fundamental aspects of heterogeneous catalysis, researchers have recognized the need to address various technical gaps relating fundamental observations under pristine conditions to factors affecting the working catalyst.Some of those observations scale, and others do not, but in both cases the atomic/molecular scale understanding obtained from research bridging those divides has been invaluable to the advancement of heterogeneous catalysis as practiced.Nevertheless, significant technical gaps still exist in advancing catalyst technology through the concept, design, and development stages to commercial application.Catalyst technology often gets stuck at a particular level, characterized by a combination of factors best described as “knowledge gaps.”At that point, industry tends to focus on optimization around a core (often proprietary) technology, and the academic community heads off to new pastures.Federal funding agencies and our national laboratories sit in a unique position to forge research partnerships between academic and industry researchers that bridge knowledge gaps.I will provide specific examples of key knowledge gaps in heterogeneous catalysis, and how NSF is funding partnerships between academic institutions and industry to bridge those gaps.

3:05pm **LI-TuA1-28 Closing Remarks and Thank You's*, Zhenrong Zhang,*** Baylor University

Thank you for attending today's session! We look forward to seeing you tomorrow at 10:00 am EDT for a full day of Live Parallel Sessions. Remember to check out the AVS 67 On Demand Sessions which are available in the mobile app and online scheduler.

Live Session
Room Live-2 - Session LI-TuA2

Tuesday Afternoon Live Session II: Novel Characterization and Modeling

Moderators: Mohan Sankaran, University of Illinois at Urbana-Champaign, Virginia Wheeler, U.S. Naval Research Laboratory

12:50pm **LI-TuA2-1 Welcome and Opening Remarks*, Ginger Wheeler,*** U.S. Naval Research Laboratory

Welcome to the AVS 67 Virtual Symposium! We hope you will enjoy the event!

12:55pm **LI-TuA2-2 Time-Resolved Photoelectron Spectroscopy of Solar Cell Materials*, Ute Cappel,*** KTH - Royal Institute of Technology, Sweden **INVITED**

Solar cells have a great potential in replacing fossil fuels in electricity generation, if requirements of low production costs can be met. In the last years, much research has focused on developing new solar cells made from organic or hybrid materials, which can be fabricated by cheap methods. This includes solar cells with a hybrid organic inorganic perovskite as the active layer in the solar cell, which have now reached power conversion efficiencies of more than 25%. In a typical solar cell, the perovskite layer is sandwiched between two selective contacts, one for holes and one for electrons.

The future success of these developments crucially depends on understanding the details charge separation, charge transport and charge recombination at the interfaces between the different layers in a solar cell as well as what parameters limit solar cell stability. X-ray based techniques such as photoelectron spectroscopy (PES) are powerful tools for obtaining electronic structure information of materials at an atomic level.By varying the photon energy from soft to hard X-rays, photoelectron spectroscopy can be used for non-destructive depth profiling of the solar cell interfaces giving information about the energy alignment and chemical structure and composition at the interface.

In this presentation, I will describe how we have used photoelectron spectroscopy for time-resolved and *operando* studies of complete solar cells. I will present results, where we were able to measure PES of a complete perovskite solar cells while applying an external bias and during visible illumination. This allowed us to determine the electronic structure and energy alignment of the active layer / back contact interface of the solar cell under operating conditions. Furthermore, I will discuss how time-resolved pump-probe measurements can be used to determine electron transfer dynamics in solar cells. For this, I will give an example of measuring the electron transport times in lead sulfide quantum dots films by combining photoelectron spectroscopy with sample excitation by a visible short-pulsed laser [1]. The described methods provide new ways of gaining insights into the working mechanism of solar cells based different combinations of materials.

[1] T. Sloboda et al. ScientificReports, 10, 1-14 (2020).

1:15pm **LI-TuA2-6 Application of a Laboratory-Based Scanning XPS/HAXPES Instrument for the Characterization of Buried Interfaces*, Kateryna Artyushkova,*** *J. Mann, J. Newman,* Physical Electronics USA*; R. Inoue, K. Watanabe, H. Yamazui,* ULVAC-PHI, Inc., Japan*; A. Vanleenhove, C. Zborowski, T. Conard,* IMEC, Belgium **INVITED**

X-ray Photoelectron Spectroscopy (XPS) is a widely used surface analysis technique with many well established industrial and research applications. The surface sensitivity (top 5-10 nm) of XPS and its ability to provide short-range chemical bonding information make the technique extremely popular in materials characterization and failure analysis laboratories. While its surface sensitivity is an important attribute, in some cases, the depth of analysis of XPS is not sufficient to analyze buried interfaces without first sputter etching the sample surface. However, sputter etching can often lead to alterations of the true surface chemistry. An alternative to sputter etching the sample is Hard X-ray Photoelectron Spectroscopy (HAXPES), available at some synchrotron facilities. HAXPES utilizes X-rays typically defined as having energies greater than 5 keV. By increasing the photon energy of the X-ray source, the mean free path of photoelectrons is increased, resulting in an increased information depth obtained from the sample. Depending on the energy used, these hard X-rays can provide depths of analysis three or more times than that of soft x-rays used on conventional XPS systems. HAXPES measurements are, therefore, more sensitive to the bulk, and contributions from the surface are minimized.[1,2]This presentation will describe a laboratory-based instrument, the PHI *Quantes*, equipped with two scanning microprobe monochromated X-ray sources, Al Kα (1486.6 eV) and Cr Kα (5414.7 eV), thus enabling both traditional XPS and HAXPES experiments in the same instrument. By combining both soft and hard X-ray analyses, we can gain an even better understanding of composition with depth and information at buried interfaces.

References

1. Kobayashi, K. Hard X-ray photoemission spectroscopy, *Nucl. Instr. Meth. Phys. Res. A* **2009**, 601, 32-47.

2. Fadley, C.S. Hard X-ray Photoemission: An Overview and Future Perspective. In Hard X-ray Photoelectron Spectroscopy (HAXPS); Woicik, J. C., Ed; Springer: Switzerland 2016.

1:35pm **LI-TuA2-10 Precise Ion Energy Control With Tailored Waveform Biasing: Determination of Sputter Thresholds as Input for ALE Process Design**, ***Nicholas Chittock****, S. Balasubramanyam, T. Faraz, Y. Verstappen,* Eindhoven University of Technology, Netherlands*; M. Verheijen,* Eurofins Materials Science , Netherlands*; J. Escandon-Lopez, E. Heijdra, W. van Gennip,* Prodrive Technologies, Netherlands*; E. Kessels, A. Mackus,* Eindhoven University of Technology, Netherlands **INVITED**

Anisotropic atomic layer etching (ALE) relies on the use of directional ions having an energy within a specific ion energy window to remove a modified surface layer.[1] The selectivity and etch control of ALE depend strongly on the ability to limit the ion energy within this window. However, tuning of the ion energy is often achieved by application of a radio-frequency sinusoidal bias voltage waveform to the substrate, which results in a relatively broad ion energy distribution leading to a loss of selectivity.[2] In this work, we report on employing tailored waveform bias voltages to accurately control the ion energy during ALE.

A prototype bias voltage generator from Prodrive Technologies was used to produce tailored bias waveforms consisting of a voltage pulse and a ramp. Narrow energy distributions (< 7 eV FWHM) were demonstrated for ion energies up to 200 eV, as measured using a retarding field energy analyzer (RFEA) in collisionless Ar plasmas.[3] By using a low-frequency (100 kHz) waveform, independent control of the ion energy and ion flux was obtained.

Tailored waveform biasing enables precise determination of sputter thresholds which can serve as an input for ALE processes with high synergy and selectivity.[1] Al_2O_3 and HfO_2 sputter thresholds were determined in an Ar plasma as 59 ± 5 eV and 81 ± 5 eV, respectively. Surface modification by SF_6 plasma exposure generated a fluorinated surface layer on the Al_2O_3 and HfO_2 films. Fluorination resulted in an increase in sputter yields as well as a reduction of the sputter thresholds to 23 ± 4 eV and 37 ± 4 eV, respectively. Evaluating the sputter yield as a function of time shows that an initially higher sputter yield returns toward that of the bulk, indicating full removal of the modified layer. Using this knowledge, an Al_2O_3 ALE process consisting of SF_6 plasma and Ar plasma exposures was evaluated. This work demonstrates that combing self-limiting surface reactions with accurate ion energy control can offer a route to precise and selective ALE.

11. K. J. Kanarik, et al., J. Phys. Chem. Lett., 9, 4814–4821. (2018)
12. S. B. Wang & A. E. Wendt, J. Appl. Phys., 88, 643. (2000)
13. T. Faraz et al., Journal of Applied Physics, 128, 213301 (2020)

2:05pm **LI-TuA2-16 Going Beyond Superficial Surface Analysis for Transforming Plants into Value-added Products**, ***Robyn Goacher,*** Materion Corp. **INVITED**

Preparation of biofuels and value-added bioproducts from lignocellulosic plant matter is an important part of moving away from our global reliance on fossil fuels. Surface analysis of the solid plant starting materials and end products can be complicated by residues from the required chemical or enzymatic treatments and by overlapping signals from plant components themselves. Peak pattern analysis by multivariate statistical approaches such as principle components analysis (PCA) is vital to identifying contaminants from buffers, plasticizers, tape supports, etc, and for distinguishing between fragment ions shared by extractive compounds such as waxes and the main plant biopolymers of cellulose, hemicellulose and lignin. This talk suggests best practices in sample preparation, choice of controls, collection of replicates, and data analysis for lignocellulosic analysis by ToF-SIMS. Accomplishments and gaps in our knowledge of characteristic ions for plant components are described, along with examples of how ToF-SIMS has been used to describe the activity of purified enzymes on wood, fungal activity on wood, and chemical treatments of plant matter.

2:25pm **LI-TuA2-20 Molecular Dynamics Study on Damage Formation in Atomic Layer Etching of Si With Halogen Radicals**, ***Erin Joy Capdos Tinacba****, M. Isobe, S. Hamaguchi,* Osaka University, Japan **INVITED**

Atomic layer etching (ALE) has gained much attention in the past years as an essential technique in fabrication processes of nano-scale semiconductor devices. ALE is a technique to achieve an atomic-scale control of an etching process by separating it into two steps; adsorption and desorption. In the adsorption step, the surface is modified by depositing a mono-layer or thin layer of less reactive molecules. In plasma enhanced ALE (PEALE), the modified layer is removed in the desorption step with the bombardment of energetic ions such as Ar^+. Ideally these ions should not be energetic enough to continuously etch an unmodified or a clean surface. This is called a self-limiting process of ALE. However, more often than not, non-ideal ALE, i.e., ALE without a complete self-limiting process, is utilized in semiconductor fabrication. In non-ideal ALE, more than one monolayer is removed and the sub-layer of the material may be damaged by excessive ion bombardment. Such damages can be critical on some electronic properties of the materials.

In this work, molecular dynamics (MD) simulation [1] was employed to have a deeper understanding of the reaction mechanisms and damage formation during ALE of Si with F, Cl, or Br adsorption and low-energy Ar^+ ion bombardment. The Ar^+ ion energy was varied from 20 to 60 eV. Five cycles of adsorption and desorption steps were simulated and the results were compared with experimental observations [2-4]. It was found that the etch-per-cycle (EPC) value was typically lower during the first cycle compared to the succeeding cycles because the first cycle was mostly spent for the formation of a modified layer. After the first cycle, a reproducible EPC value was observed. The effects of Ar^+ ion bombardment on the modified surface as well as its Si sub-layer were also investigated. It was observed that, even at low Ar^+ ion incident energy (20 – 30 eV), the Si sub-layer is damaged in the desorption step and the extent of this damage increases with increasing energy.

[1] E. J. C. Tinacba, *et al.*, Surf. Coat. Technol. 380 (2019), 125032.

[2] H. Sakaue, *et al.*, Mat. Res. Soc. Symp. 222 (1991), 195.

[3] S.-D. Park, *et al.,* Jpn. J. Appl. Phys. 44 (2005), 389.

[4] S. Tan, *et al.,*ECS J. Solid State Sci. Technol., 4(6) (2015), N5010-N5012.

2:45pm **LI-TuA2-24 Variable Polarization, External Magnetic Field, and Spin Resolution for Buried Magnetic Materials Studied by Hard X-Ray Photoemission**, ***Shigenori Ueda,*** National Institute for Materials Science, Japan **INVITED**

Hard X-ray photoemission spectroscopy (HAXPES) with variable X-ray polarization is useful tool for studying the electronic structures of solids [1,2]. By using horizontal and vertical linear polarized X-ray, the valence band HAXPES spectra show the strong polarization dependence, which allows us to atomic orbital dependent electronic states [1]. For the magnetically ordered materials, HAXPES with left and right handed circularly polarized X-rays permits to probe the magnetic information form the magnetic circular dichroism in core-level photoemission in the element specific way [2]. Since HAXPES is known as a bulk-sensitive probe for electronic structures of solids due to large inelastic mean-free-path of photoelectrons with several keV, it is now possible to probe the electronic states of buried interfaces. In this presentation, the electronic and magnetic states of MgO/Fe interfaces are studied by HAXPES under an applied magnetic field using variable X-ray polarization [3]. The used samples are MgO(2 nm)/Fe(1.5 and 20 nm)/MgO(001), in which the thick and thin Fe films exhibit the in-palne and perpendicular magnetic anisotropies, respectively. For the thin Fe film, the electronic states of the top and bottom interfaces can be probed by HAXPES, while the electronic states of the Fe film inside are dominant in HAXPES. The role of the MgO/Fe interfaces and interface-induced magnetic anisotropy are discussed by comparing the density functional theory calculations. And I will show the results of high-throughput depth-resolved HAXPES combined with total reflection [4] for the MgO(2 nm)/Fe(50 nm)/MgO(001) and spin-resolved HAXPES for buried Fe films [5].

References

[1] S. Ueda and I. Hamada, J. Phys. Soc. Jpn. 86 (2017) 124706.

[2] S. Ueda et al., Appl. Phys. Express 1 (2008) 077003.

[3] S. Ueda et al., Sci. Technol. Adv. Mater. 20 (2019) 796.

[4] S. Ueda, Appl. Phys. Express 11 (2018) 105701.

[5] S. Ueda and Y. Sakuraba, Sci. Technol. Adv. Mater. under review.

3:05pm **LI-TuA2-28 Closing Remarks and Thank You's***, Mohan Sankaran,* University of Illinois at Urbana-Champaign

Thank you for attending today's session! We also look forward to seeing you tomorrow at 10:00 am EDT for a full day of Live Parallel Sessions. Remember to check out the AVS 67 On Demand Sessions which are available in the mobile app and online scheduler.

Live Session

Room Live - Session LI-WeM1

Wednesday Morning Live Session I: Recent Advances in Thin Films

Moderators: Svitlana Pylypenko, Colorado School of Mines, Angel Yanguas, Argonne National Lab

10:00am **LI-WeM1-1 Welcome and Opening Remarks*, Angel Yanguas-Gil,*** Argonne National Lab

Welcome to the AVS 67 Virtual Symposium! We hope you will enjoy the event!

10:05am **LI-WeM1-2 Metalorganic Vapor-Phase Epitaxy of Gallium (Aluminum) Oxide Thin Films and Heterostructures for High Frequency and Power Electronics*, Sriram Krishnamoorthy,*** University of California, Santa Barbara*; P. Ranga, A. Bhattacharyya, S. Roy,* Electrical and Computer Engineering, The University of Utah **INVITED**

Beta- Gallium Oxide (β-Ga_2O_3) is an emerging ultra-wide band gap (UWBG) material with the availability of high quality native substrates grown using potentially inexpensive melt-based techniques. In this talk, I will highlight the tremendous progress made by the Gallium Oxide research community in the last few years, in the area of metal-organic vapor phase epitaxy (MOVPE).

In the first part of the talk, I will focus on our group's first demonstration of delta doping and modulation-doped Aluminum Gallium Oxide/ Gallium Oxide heterostructures grown using metal organic vapor-phase epitaxy (MOVPE) towards achieving high electron mobility. Growth of delta-doped (010) β-Ga_2O_3 films is performed by Agnitron Agilis MOVPE reactor with TEGa, O_2 and silane as precursors and argon as carrier gas. Delta doping of β-Ga_2O_3 is achieved by interrupting the growth of β-Ga_2O_3 and supplying silane to the reactor with purge steps before and after the flow of silane. Multiple samples are grown under varying silane flows to study silicon incorporation inβ-Ga_2O_3. CV measurements are used to characterize the sheet charge density and FWHM of the silicon delta sheet. SIMS measurements are used to estimate the concentration of silicon donor atoms in β-Ga_2O_3. Sheet charge density extracted from CV measurements is in the range of 2×10^{12} cm^{-2} and 1×10^{13} cm^{-2}. Sharp delta doping profiles are achieved by controlling the surface riding of silicon donors. Using a delta-doped β-$(Al_{0.26}Ga_{0.74})_2O_3$ barrier layer, a room temperature electron sheet charge density as high as 1×10^{13} cm^{-2} is realized at the β-$(Al_{0.26}Ga_{0.74})_2O_3$/$\beta$-$Ga_2O_3$ heterojunction. The electron sheet charge did not exhibit freeze out at 90 K, confirming degenerate behavior. This value is the highest reported degenerate electron density in β-$(Al_xGa_{1-x})_2O_3$/β-Ga_2O_3 material system.

In the second part of the talk, I will discuss MOVPE-regrown selective area ohmic contacts with resistance as low as 1×10^{-4} ohm cm^2. This is particularly enabled by the large growth temperature window of MOVPE-grown homoepitaxial (010)-oriented Ga_2O_3, resulting in excellent material growth at growth temperatures as low as 600^{o}C. These early results on delta doping, modulation doping and the large growth temperature window for β-Ga_2O_3 homoepitaxy show the potential of the MOVPE technique for achieving high quality UWBG thin film and heterostructures towards applications in high frequency and high power electronics.

10:25am **LI-WeM1-6 Selection Criteria for Small Inhibitor Molecules in Area-Selective Atomic Layer Deposition*, Marc Merkx,*** *P. Yu, J. Li,* Eindhoven University of Technology, Netherlands*; D. Hausmann,* Lam Research Corp.*; T. Sandoval,* Universidad Técnica Federico Santa Mariá, Chile*; E. Kessels, A. Mackus,* Eindhoven University of Technology, Netherlands **INVITED**

Implementing vapor-phase dosing of small inhibitor molecules in advanced atomic layer deposition (ALD) cycles is currently being considered to enable area-selective ALD. When using small inhibitor molecules, it can be challenging to completely block precursor adsorption, due the inhibitor size and the relatively short vapor-phase exposures. This work aims at providing a framework for the selection of small inhibitor molecules such that area-selective ALD with a high selectivity can be achieved. In previous work, we showed that small inhibitor molecules typically adsorb in a mixture of bonding configurations, and that not all bonding configurations block precursor adsorption equally well.[1]

Inhibitor selection requires consideration of the packing of inhibitors, inhibitor bonding configurations, the inhibitor binding strength, and intermolecular interactions. As a model system, the adsorption of acetic acid ($C_2H_4O_2$), acetylacetone (Hacac, $C_5H_8O_2$), and 2,2,6,6-tetramethyl-3,5-heptanedione (TMHD, $C_{11}H_{20}O_2$) was studied. Infrared (IR) spectroscopy shows that TMHD has the highest efficiency for blocking bis(diethylamino)silane (BDEAS) precursor adsorption. In terms of surface packing, random sequential adsorption (RSA) simulations [2] indicate that TMHD adsorbs in a lower surface density as compared to acetic acid and Hacac, but due to its larger size still covers a larger fraction of the non-growth area. Density functional theory (DFT) calculations reveal that attractive interactions with incoming BDEAS molecules, which cause a loss of selectivity when using Hacac,[1] are less likely to occur when using TMHD due to steric limitations. Correspondingly, IR spectroscopy shows less inhibitor displacement by the BDEAS precursor than for acetic acid and Hacac.

The model system suggests that using a more bulky inhibitor is beneficial for precursor blocking, as a larger size helps to shield the reactive group of the inhibitor from interacting with the incoming precursor. Overall, both the packing and stability of the inhibitor on the surface need to be as high as possible for effective precursor blocking, where the stability is affected by the bonding of the inhibitor with the surface and potential interactions with incoming precursors. The mechanisms that affect precursor blocking will be discussed within a framework for selecting small inhibitor molecules.

[1] Merkx *et al., Chem. Matter.***32**, 3335 (2020)

[2] Khan *et al., Chem. Matter.***30**, 7603 (2018)

10:45am **LI-WeM1-10 Ligand-Exchange Reactions Using Silane Precursors Containing Different Ligands: Pathways for Selective Thermal Atomic Layer Etching*, Ann Lii-Rosales,*** *V. Johnson, A. Cavanagh, S. Sharma, S. George,* University of Colorado Boulder **INVITED**

The ligand-exchange reaction is an effective pathway for thermal atomic layer etching (ALE) of metal oxides. The metal oxide is usually fluorinated by HF to make metal fluoride. Then, the metal fluoride can undergo ligand-exchange reactions with a precursor molecule. Depending on the choice of ligands on the precursor, ligand-exchange can produce stable and volatile etch products. Silanes are important precursors for ligand-exchange with metal fluorides because silicon forms strong Si-F bonds. In addition, silicon can bind to a variety of ligands including CH_3, Cl, H and $N(CH_3)_2$. This study examined ligand-exchange reactions with metal fluorides using various silane precursors such as $SiCl_4$, $SiCl_2(CH_3)_2$ and $SiH(CH_3)_2Cl$. The investigations were performed with *in situ* mass spectrometry experiments to detect the ligand-exchange products and etch species during temperature ramps from 30-520°C.

For the reaction of $SiCl_4$ with SnF_4 powder, $SiCl_4$ was observed to undergo complete F-Cl exchange with SnF_4 powder to produce SiF_4. The F-Cl exchange also produced $SnCl_4$ as the volatile etch species at 150°C. Calculations of the sequential ligand-exchange required to convert SnF_4 to $SnCl_4$ also confirmed the favorability of these reactions. In contrast to $SiCl_4$, $SiCl_2(CH_3)_2$ has both Cl and CH_3 ligands that can be involved in ligand-exchange. The reaction of $SiCl_2(CH_3)_2$ with SnF_4 powder produced $SiF_2(CH_3)_2$, and $SnCl_4$and $SnFCl_3$ as etch species. No CH_3-containing Sn species were observed in the mass spectra indicating the preference of F-Cl ligand-exchange. In addition, $SnCl_4$ etch species did not appear until a much higher temperature of 300°C. This may be attributed to the lower Cl content in $SiCl_2(CH_3)_2$.

$SiH(CH_3)_2Cl$ contains Cl, CH_3 and H ligands that may be involved in ligand-exchange. The mass spectra revealed that $SiF_2(CH_3)_2$ was the ligand-exchange product with SnF_4 powder. $SiF_2(CH_3)_2$ was observed at 150°C and indicates both F-Cl and F-H exchange. In contrast, the SnH_2Cl_2 etch product was not detected until 350°C. HF was monitored throughout the temperature ramp and H_2 was also observed at $T > 400$°C. These products clearly indicate that H is transferred to the SnF_4 powder. Moreover, *ex situ* XPS measurements of the SnF_4 powders after ligand-exchange revealed the presence of metallic Sn. This indicates that the H on the precursor molecule can serve as a reducing agent. The reactions between silanes with SnF_4 and other metal fluoride powders are revealing the details of the ligand-exchange reactions during thermal ALE. These details can lead to pathways for selective thermal ALE by varying the temperature and ligands on the precursor molecule.

11:15am **LI-WeM1-16 Superconformal Trench Filling With $Hf_{1-X}V_XB_2$ Using Two-Precursor Chemical Vapor Deposition*, Kinsey Canova,*** *Z. Zhang, G. Girolami, J. Abelson,* University of Illinois at Urbana Champaign **INVITED**

Seamless filling of deep recessed features is an ongoing challenge in the fabrication of advanced microelectronic devices.We demonstrate a new CVD method that affords superconformal films (i.e., faster growth deeper in the feature) based on the use of two precursor molecules with sharply contrasting adsorption and reaction properties.One precursor adsorbs strongly but reacts relatively slowly; the other precursor adsorbs less strongly but reacts more rapidly. The strongly adsorbing precursor inhibits the overall growth rate, but it is progressively consumed along the trench sidewalls.Consequently, the inhibition effect diminishes and fast growth from the second precursor affords an increase in growth rate with trench depth.The resulting thickness profile is superconformal (V-shaped), which leads to seamless fill.We show that the needed adsorption and reaction kinetics exist using $V(N(CH_3)_2)_4$ as the inhibiting precursor and $Hf(BH_4)_4$ as the second precursor; together, these afford films of the refractory metallic ceramic $Hf_{1-x}V_xB_2$. Under practical growth conditions, we obtain seam-free filling up to a depth-to-width (aspect) ratio of 10.

We model the kinetics based on the dependence of the film growth rate and composition *x* on the local pressure (flux) of each precursor, with ballistic transport of precursor between surfaces within the trench.The model uses a Langmuirian framework in which precursors compete for available adsorption sites and adsorbates have different reaction rates.The model shows that there is a limiting aspect ratio for a given set of kinetic coefficients.Here, the growth of $Hf_{1-x}V_xB_2$ facilitates comparisons with the model because the film composition varies with depth; this compositional change reflects the changes in the surface coverage and reaction rate of each precursor as the gas phase composition changes with depth.In future work, it will be desirable to use two precursors that afford the same film, so that the resulting composition will be uniform within the trench.We will suggest precursor combinations that are good candidates for superconformal trench filling with other technologically-relevant materials.

11:35am **LI-WeM1-20 Pyroelectric Heat Detection for *In Situ* Measurement of ALD Reaction Heat*, Ashley R. Bielinski,* *E. Sprague-Klein, B. Phelan, A. Martinson,* Argonne National Laboratory **INVITED**

Atomic layer deposition (ALD) is used to deposit a wide range of materials for both academic and industrial applications, yet experimental resolution of the kinetics, thermodynamics, and mechanisms for even the most well-studied ALD half-reactions remains insufficient to test computational models.*In situ* measurements of the heat generated by ALD half-reactions could provide new insight into the complex chemical processes at play during ALD. ALD reactions have been observed to cause >10°C temperature changes on high surface area substrates like nanoparticles or metal organic frameworks, but the relatively small temperature changes (<0.1°C) predicted for planar substrates are much more difficult to accurately measure.Additionally, many reactions exhibit kinetics that are on the same order as or faster than the 10ms to 1s sampling times of *in situ* measurement techniques commonly used for ALD such as mass spectrometry, ellipsometry, or quartz crystal microgravimetry.

We present a pyroelectric calorimeter with thermal and temporal resolution down to 0.1 $\mu J/cm^2$ and 50 ns.This probe enables the time-resolved measurement of individual ALD half-cycles, enabling comparison to first-principles computational predictions.The calorimeter hardware was designed and optimized for operation under ALD conditions.Laser calibration was combined with a mathematical model of the transient thermal and electrical response to provide quantitative measurements of heat generation rates.Trimethylaluminum (TMA) was reacted with a planar, hydroxylated ALD-alumina surface to produce 96 $\mu J/cm^2$ over a reaction time of ~30 ms.Relative to other in situ measurement techniques, calibrated pyroelectric calorimetry offers a faster and more sensitive probe of ALD reactions.In addition to kinetic and thermodynamic measurements of steady state growth reactions, this technique may also provide the necessary precision to study the complexities and far sub-monolayer growth during nucleation or selective deposition.

This material is based upon work supported by Laboratory Directed Research and Development (LDRD) funding from Argonne National Laboratory, provided by the Director, Office of Science, of the U.S. Department of Energy under Contract No. DE-AC02-06CH11357

11:55am **LI-WeM1-24 pH Sensor Tattoo*, Katrin Unger*,** *A. Coclite, F. Greco,* Graz University of Technology, Austria **INVITED**

Temporary tattoo-based body sensors have gained high attention in the expanding field of tracking physiological biomarkers, such as the pH level of sweat. Because of its ultra-conformal adhesion towards the skin while providing excellent water vapor transmission, temporary tattoo sensors can react already at minimal sweat production but can also cope with large amounts of sweat. Within the presented work, a skin pH sensor tattoo is presented, made of a temporary tattoo paper, screen printed polymer electrodes and a pH responsive hydrogel. While so far tattoo papers have been functionalized only by solution-based methods, within this study for the first time a vapor-based coating routine, named initiated chemical vapor deposition, was utilized to deliver a smart hydrogel. The resulting sensor tattoo can be easily transferred on the skin and shows an outstanding conformability to the topography of the epidermis. The measured morphology properties of the layers demonstrate excellent process controllability of the desired electrode width, hydrogel thickness and shielded areas. The pH responsive hydrogel exhibits a reversible pH responsive swelling of 24% to 37%, in respect to the dry state, at pH 4 and pH 6, respectively. With impedance spectroscopy the phase shift at 1000 Hz is identified as an excellent pH-related parameter of the sensor, which can only be ascribed to the presence of the hydrogel layer. The sensor can be triggered and read out also by a cheap and light-weight Arduino setup, verifying the applicability as a wearable sensor device.

12:15pm **LI-WeM1-28 Closing Remarks and Thank You's*, Svitlana Pylypenko,*** Colorado School of Mines

Thank you for attending today's session! Please note that our afternoon sessions begin at 12:50 pm EDT. Remember to check out the AVS 67 On Demand Sessions which are available in the mobile app and online scheduler.

Live Session
Room Live-2 - Session LI-WeM2

Wednesday Morning Live Session II: Biological, Environmental Interfaces and New Directions in the AVS

Moderators: Sidney Cohen, Weizmann Institute of Science, Israel, Caitlin Howell, University of Maine

10:00am **LI-WeM2-1 Welcome and Opening Remarks*, Sidney Cohen,*** Weizmann Institute of Science, Israel

Welcome to the AVS 67 Virtual Symposium. We hope you will enjoy the event!

10:05am **LI-WeM2-2 ASSD 2021 Peter M.A. Sherwood Mid-Career Professional Award Talk: Information from complexity - Making Sense of the Mess Created by ToF-SIMS*, Daniel Graham*[1]**, University of Washington, Seattle*; M. Taylor,* Pacific Northwest National Laboratory*; L. Gamble,* University of Washington, Seattle **INVITED**

ToF-SIMS data from even simple surfaces is complicated. This complexity is a blessing and a curse as it encodes information about the structure and composition of surface molecules and presents a massive data processing challenge to decode this information from within the hundreds of spectral peaks present in a typical spectrum. This challenge is further complicated by the fact that modern ToF-SIMS instruments can produce sub-micron resolution images where each pixel contains a full mass spectrum. This imaging modality can be combined with sputtering beams to enable depth profiles of materials which can contain multiple images acquired throughout the depth of a material. The result of this is a chemically rich, spatially mapped data matrix containing information about the chemistry, location, structure and composition of surface species. Such data matrices can contain tens of thousands (2D data) to millions (3D data) of spectra taking up 10s to 100s of GB. The challenge then becomes how to process this data and extract the gems of information encoded within the fragmentation patterns of each spectrum. To address these issues many researchers have applied a wide variety of multivariate and other advanced data analysis methods to ToF-SIMS data in order to extract useful information that can be used to aid in materials characterization.

In spite of this complexity, ToF-SIMS has found wide application in the analysis of organic and biological materials as it presents a method that can provide specific chemical information and precise localization of surface compounds.This can be particularly useful in the analysis of biomaterials, where understanding of the surface chemistry is critical to device success, and in the analysis of cells and tissues where mapping chemical changes can elucidate information that can be useful in understanding disease progression and possibly prevention.

In this talk I will demonstrate how the application of multivariate, and other advanced analysis methods, can facilitate digesting ToF-SIMS data and extracting useful information that can help solve problems in organic and biological materials characterization.Examples will be shown from spectral and image analysis (2D and 3D), along with ways we have explored

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[1] **ASSD 2021 Peter M. A. Sherwood Mid-Career Professional Awardee**

to enable the characterization of topographically challenging samples used in tissue engineering.In addition I will highlight the importance of sharing tools developed for this type of analysis and describe tools we have created to facilitate multivariate analysis throughout the scientific community.

10:25am **LI-WeM2-6 High Throughput Discovery of Novel Antiviral Polymers for Reducing SARS-CoV-2 Surface Transmission and Improving PPE*, Xuan Xue*,** *J. Duncan, C. Coleman, J. Ball, C. Alexander, M. Alexander,* University of Nottingham, UK **INVITED**

Respiratory diseases caused by viruses have become a serious global public health concern. The ongoing COVID-19 global pandemic has threatened people's lives and impacted socioeconomical development since December 2019. To date, Severe Acute Respiratory Syndrome Coronavirus 2 (SARS-CoV-2) appears to spread easily in droplets in the air and via surfaces. Following evidence of virus contamination of surfaces, the fomite transmission of respiratory viruses has been highlighted as a potential infection route in the pandemic. In addition, healthcare workers in the front line of the COVID-19 outbreak response are exposed to the risk of SARS-CoV-2 infection daily. Personal protective equipment (PPE) is their main defence against viral contamination and to eliminate viral transfer from infected patients. Antiviral effective PPE materials, that can be self-disinfected and ideally worn for prolonged time, need to be developed.

In our study, a range of commercially available PPE materials and common surface plastics have been evaluated using live virus in Biosafety Level 3 (BSL-3) laboratory to enable a recommendation of which existing polymers should be employed for optimal viral inactivation on PPE. Detachment assays using virus like particles (VLPs), which do not have an infection risk, were used to investigate secondary spreading of viruses invoked by movement and doffing of PPE with both liquid and air flow systems explored to mimic actual environmental conditions. The persistence of live SARS-CoV-2 on these surfaces were evaluated and compared under varied temperature and relative humidity conditions.

In order to develop new polymers for PPE and fomite transmission control, high throughput polymer microarrays developed at the University of Nottingham, were used to identify novel anti-SARS-CoV-2 polymer materials.

10:45am **LI-WeM2-10 Machine-Learning-Assisted Photonics***, Z. Kudyshev, A. Kildishev, V. Shalaev,* ***Alexandra Boltasseva*,** Purdue University, USA **INVITED**

We coupled adversarial autoencoder deep generative network with adjoined topology optimization technique to advance metasurface design. The proposed approach speeds up the optimization search of highly efficient metasurface designs and also provides unparalleled control over the compressed design space distribution. The latter fact assures scalability of the approach to highly-constrained optimization problems.

Nanophotonics can provide solutions to interdisciplinary challenges in energy [1], quantum IT [2] and other areas. Addressing multifaceted problems require highly-constrained optimization of the device design, due to inherent complexity and multi-disciplinary nature of any practical application. Conventionally, adjoint [3] and genetic [4] optimization methods have been used to address such optimization tasks. However, the computational power requirement of these methods scales up with the number of constraints. This fact substantially limits the applicability of conventional optimization techniques to real-life applications. Within this work, we merged the adjoint topology optimization technique with adversarial autoencoders (AAE) to achieve significant improvement in the optimization search of non-trivial nano-antenna-based metasurface designs [5]. Particularly, we demonstrated that the proposed approach ensures not only the efficient optimization search of high-performance metasurface designs but also provides unparalleled control over the compressed design space distribution. The latter fact assures scalability of the approach to highly-constrained optimization problems. To showcase AAE-assisted method, we optimized a metasurface thermal emitter for thermophotovoltaic (TPV) applications. Compared to an adjoint-based topology optimized design with 92% efficiency of the thermal emission reshaping, the proposed method provides three times speed-up and gives 98% efficiency. The proposed approach can be adapted to a broader scope of the problems in optics.

References

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11:15am **LI-WeM2-16 STM Measurements of Spin-Polarized Currents Carried by the Topological Surfaces States of SmB_6 Nanowires*, Vidya Madhavan,*** University of Illinois at Urbana-Champaign **INVITED**

Incorporating relativistic physics into quantum tunneling can lead to exotic behavior such as perfect transmission via Klein tunneling, or apparent faster than light travel. In this talk I will describe an experiment that demonstrates `helical tunneling', a process where spin-polarized electrons can be transmitted in a nominally time-reversal invariant fashion. To do this we use nanofabrication techniques to attach SmB_6 nanowires to the end of scanning tunneling microscope tips. SmB_6 is a topological Kondo Insulator which has been proposed to be an ideal topological system with Dirac fermions naturally dominating the density of states near Fermi level. The SmB_6 nanowire tips are used to image the canonical spin density wave material, $Fe_{1.03}Te$, which hosts a bicollinear spin order with a Neel temperature of ~50 K. STM images show a superstructure with the periodicity of the antiferromagnetic order, indicating spin-selective tunneling from the nanowire. The antiferromagnetic order becomes invisible above 10 K, far below the Neel temperature, together with the diminishing topological surface states. We further confirm a smoking gun signature of spin current generated by Dirac fermions, i.e., the contrast reversal of the antiferromagnetic order at opposite bias voltages. These findings establish interacting topological systems like SmB_6 as ideal conduits for spin-polarized topological currents and reveal an unexpected and unexplored consequence of relativistic tunneling.

11:35am **LI-WeM2-20 Molecular Nanostructures on Metals vs. Graphene: Towards Preserving Functional Properties*, Meike Stöhr,*** University of Groningen, Netherlands **INVITED**

To preserve the (functional) properties of either individual adsorbates or well-ordered molecular assemblies upon adsorption on solid surfaces, the molecule substrate interactions have to be generally relatively weak. This can be achieved by introducing a decoupling layer between (metallic) surface and molecules. Among others, thin insulating layers of either NaCl or a single layer of hBN have been shown to be very useful to this end. The chemical inertness and the low density of states near the Fermi level also make graphene a good choice as a buffer layer to decouple adsorbed molecules from the underlying (metallic) substrate. Importantly, this holds the promise to preserve the intrinsic properties of the adsorbed species such as magnetic or catalytic properties. On the other hand, molecular self-assembly on graphene can be also employed as a promising method for tuning the electronic properties of graphene (doping or band gap opening) on a macroscopic scale while for this purpose, the molecule graphene interaction has to be larger than a mere physisorptive one.

Here we will discuss the structural and electronic properties for 1,3,5-benzenetribenzoic acid on graphene/Cu(111), for which different coverage dependent assemblies were observed. [1] We could demonstrate that the underlying Cu surface influences the structural arrangement of the molecules. With respect to the electronic properties, angle-resolved photoemission spectroscopy measurements showed n-doping of graphene. For parahexaphenyl-dicarbonitrile ($NC-Ph_6-CN$) on graphene, we observed the arrangement of a close-packed structure with a peculiar shift of every 4th molecule independent of coverage. We concluded that the screening properties of graphene are responsible for this effect since such a shift was neither observed for the case of metallic substrates nor for the bulk phase. [2] Adding Cu adatoms to submonolayer coverage of $NC-Ph_6-CN$ resulted in the formation of metal-organic coordination networks with varying arrangements in dependence of the stoichiometry between molecules and Cu atoms. With scanning tunneling spectroscopy we characterized the electronic properties and could identify differences between the different assembly structures. [3] On the basis of the self-assembly process of tetracyanophenyl porphyrins before and after coordination with Co-atoms on Au(111), the influence of molecular coverage on decoupling could be demonstrated. [4]

[1] J. Li et al., J. Phys. Chem. C 120 (2016) 18093; N. Schmidt et al., unpublished.

[2] N. Schmidt et al., Chem. Eur. J. 25 (2019) 5065.

[3] J. Li et al., J. Phys. Chem. C 123 (2019) 12730.

[4] B.D. Baker et al., J. Phys. Chem. C 123 (2019) 19681.

11:55am **LI-WeM2-24 BID 2020-2021 Early Career Awardee Talk: Molecular-Level Insights Into Novel Wet Adhesion Systems Found in the Natural World*, Joe Baio*[1]*,* Oregon State University **INVITED**

From sticky frog tongues to the superhydrophobic cuticles of springtails - the natural world is full of novel materials. Recent developments of surface analytical methods now allow provide a means of characterizing the structure and arrangement of molecules at complex biological interfaces. Many animals have adapted to a range of environmental surfaces by evolving a wet adhesion process. Previous studies of these adhesion mechanisms have focused almost exclusively on the mechanical and kinematic aspects of adhesion, and not on the molecular interactions at the fluid – substrate interface. In the work presented here, we first probe the molecular interactions between the adhesive fluid taken from lady beetles (*Cocinella septempunctata*) on two model substrates (one polar and one non-polar) with vibrational sum frequency generation (SFG) spectroscopy. The resulting SFG spectra demonstrate that during adhesion to a polar surface, fatty acids within the fluid form a highly ordered layer at the substrate surface. While on a non- polar surface, the mechanism changes and some other hydrocarbon species present within the fluid orders at the interface. The discussion will then be expanded to include some recent experiments identifying the structure of the biomolecules that make up the wet adhesive mechanism molecules present at a frog’s tongue. Frogs capture their prey with a highly specialized tongue. Recent studies indicate this tongue is covered with fibril-forming mucus that acts as a pressure sensitive adhesive. However, no analysis of the interfacial chemistry of frog tongue mucus has been performed.Previous studies of mucus from other animals suggest that mucus from a frog's tongue consists of mucins—serine-, threonine-, and proline-rich glycoproteins. Therefore, the authors expect to observe chemical bonds associated with glycoproteins, as well as fibrils formed at the mucus–tongue interface. To test this hypothesis, we collected both near-edge x-ray absorption fine structure (NEXAFS) microscopy images and SFG vibrational spectra from layers of mucus left after frog tongue strikes on cleaned glass slides. NEXAFS imaging demonstrates a uniform distribution of amide, hydroxyl, and carbon–carbon bonds across the mucus surface. SFG spectra reveal that glycoproteins are well-ordered at the mucus–tongue interface.

12:15pm **LI-WeM2-28 Closing Remarks and Thank You's*, Caitlin Howell,*** University of Maine

Thank you for attending today's session! Please note that our afternoon sessions begin at 12:50 pm EDT. Remember to check out the AVS 67 On Demand Sessions which are available in the mobile app and online scheduler.

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[1] **BID 2020-2021 Early Career Researchers Award**

Live Session
Room Live - Session LI-WeA1

Wednesday Afternoon Live Session I: Controlling Matter at the Ultimate Limits

Moderators: Eric Joseph, IBM T.J. Watson Research Center, Arthur Utz, Tufts University

12:50pm **LI-WeA1-1 Welcome and Opening Remarks*, Eric Joseph,*** IBM T. J. Watson Research Center

Welcome to the AVS 67 Virtual Symposium! We hope you will enjoy the event!

12:55pm **LI-WeA1-2 The Development of Atomic Layer Processes for Scaling & Future Device Architectures*, Rudy Wojtecki,*** International Business Machines (IBM) - Almaden Research Center **INVITED**

A major aspect governing progress in electronic technologies is the ability to control or guide the deposition or subtraction of thin films.As the semiconductor community continues scaling, interfaces and surfaces become increasingly important. Traditional deposition and subtraction methods then may not be sufficient in future technology nodes as they may damage or amorphize surfaces to an otherwise crystalline and risk device performance or yield.Atomic layer processes present methods to preserve these interfaces by taking advantage of surface reactivities to either add or subtract a material one atomic layer at a time.Furthermore, these offer the opportunity to more broadly extend fabrication capabilities that may enable integration schemes for alternative computing architectures such as neuromorphic type devices.Within this space area selective depositions (ASD) offer a powerful tool to direct film growth from a chemically distinct surface in a self-aligned process with the potential to relax down-stream processing such as overlay requirements. There are many examples for the integration of these techniques to encapsulate and inhibit the oxidation of a metal or introduce surface topography from an underlying pre-pattern, for instance. Guiding this deposition is particularly challenging as it requires the careful interplay between deposition precursors and inhibiting (or activating) layers. Achieving this control, through judicious design and engineering of a surface affords exquisite control over the film characteristics such as composition and thickness.The development of processes that extend these capabilities will be discussed that include strategies to enable ASD with surface topography using an area selective polymerization that provides control over inhibitor thickness which acts as an effective inhibiting material.In addition, the combination of ASD with a patternable organic monolayer will be discussed that provides a versatile additive lithography platform, where a broad range of desired feature geometries can be readily generated.In the pursuit of methods to broaden the application of ASD processes fundamental insights to desirable material characteristics for these processes are useful parameters to consider in future ASD processes such as supramolecular interactions between inhibitors and chemical crosslinking.

1:15pm **LI-WeA1-6 Recent Innovations in Tof-Sims and Their Industrial Applications*, Julia Zakel,*** IONTOF GmbH, Germany **INVITED**

Time-of-flight secondary ion mass spectrometry (TOF-SIMS) is known to be an extremely surface sensitive analytical technique. It provides detailed elemental and molecular information about surfaces, thin layers, interfaces, and full three-dimensional analysis of the sample.In our contribution we will provide an overview on recent advances in TOF-SIMS instrumentation and data evaluation that are extending existing applications or even make new applications accessible. Among the discussed improvements are key values that are inherent for a dedicated TOF-SIMS instrument as mass resolution and lateral resolution, as well as improvements that are based on the integration of additional analytical components or due to the combination with complementary techniques.The latest technology step now pushes the standard lateral resolution of dedicated TOF-SIMS instruments to the sub 50 nm region. Best achieved values are even in the 20 nm range and therefore not far away from the physical limit given by the size of the sputter cascade. While new ion sources expanded the usability of SIMS instruments, SIMS analyzers lacked the required mass resolution and mass accuracy, required for the thorough investigation of molecular materials. One major challenge is based on the enormous number of molecules in the mass range of interest. An important step in order to reduce the number of interpretation possibilities is to improve the mass resolution and the mass accuracy. State-of-the-art TOF-SIMS instruments are reaching a mass resolution in the range of 30.000 and a mass accuracy in the range of few ppm. This improves the analytical possibilities compared to the previous instrument generation and reduces the complexity of data evaluation and interpretation.MS/MS capabilities are required in order to further increase identification possibilities. In this respect it is also of high importance to generate the MS/MS spectra at high mass resolution and high mass accuracy. We will discuss an MS/MS approach that is fully integrated into a TOF analyzer. The benefit of this approach is that it can easily be integrated in the given analysis scheme and data format.While the discussed performance represents the limit attainable with recent TOF-SIMS instruments, further improvement is achieved by combining an Orbitrap™-based mass analyzer with a high-end TOF-SIMS system (Hybrid SIMS). The instrument provides highest mass resolution (> 240,000) and highest mass accuracy (< 1ppm) with high lateral resolution cluster SIMS imaging. We will present data acquired on a Hybrid SIMS instrument demonstrating fast and robust identification of main constituents in unknown samples.

1:35pm **LI-WeA1-10 Microscopic Visualization of Electron Correlations in TMD Moiré Superlattices*, Shaowei Li,*** University of California at San Diego **INVITED**

Van der Waals heterostructures of atomically thin layered materials provide an exciting new platform to design and fabricate novel electronic and optical devices. Through the precise control of the stacking order and the twist angle between two adjacent layers, the moiré superlattice can lead to tunable narrow electronic minibands. With the unique ability to image the structural and electronic properties of low-dimensional materials at the atomic-scale, scanning tunneling microscopy and spectroscopy provide an opportunity to study the strongly correlated physics with real-space visibility. In this talk, I will present the real-space visualization of the localized correlated electron states in the closely aligned WS_2/WSe_2. These correlated states have shown the promise of exotic electron transfer properties such as charge order states, electron transfer insulator, Mott insulator, and superconductivity.

2:05pm **LI-WeA1-16 Characterizing Unconventional Strain and Bending in 2D Materials and Heterostructures with Aberration-Corrected STEM*, Pinshane Huang,*** University of Illinois at Urbana-Champaign, USA*; E. Han, J. Yu, C. Lee,* University of Illinois at Urbana Champaign*; D. Luo,* University of Illinois at Urbana Champaign*; A. Khan,* University of Illinois at Urbana Champaign*; T. Santos,* University of Illinois at Urbana Champaign*; S. Kang, W. Zhu, N. Sobh, A. Schleife, B. Clark, E. Ertekin, A. van der Zande,* University of Illinois at Urbana Champaign **INVITED**

The properties of 2D materials can be strongly impacted by the presence of defects, strain, and out-of-plane bending.In this talk, we discuss our development of techniques that use aberration-corrected scanning transmission electron microscopy (STEM) to measure the unconventional strain and bending of 2D materials and heterostructures with unprecedented precision.

First, we will discuss our studies of defect-induced strain in 2D materials. High-precision characterization of defects in 2D materials remains challenging because they are irradiation sensitive, making it difficult to achieve high resolution and signal-to-noise structural data without modifying the intrinsic structure. Here, we apply deep learning techniques based on convolutional neural networks to process large volumes of atomic-resolution images of the 2D transition metal dichalcogenide $WSe_{2-x}Te_{-x}$. By class-averaging hundreds of nominally identical defects, we measure the local picometer-scale strain fields around single vacancies with 0.2 picometer precision, and we observe previously-unseen radial strain oscillations [1].

Second, we will discuss bending in 2D materials and heterostructures.Understanding the bending of two-dimensional materials and heterostructures is crucial for the development of next-generation electronics including deformable electronics, and nanoelectromechanical systems. Here, we show that electron microscopy can provide a powerful platform for measuring the bending of 2D materials. We use aberration-corrected STEM to image graphene and 2D heterostructures draped over atomically sharp hexagonal boron nitride steps. This approach enables atomic-resolution studies of their bending conformation, producing insight into both the bending stiffness and mechanisms of bending. We find that the bending stiffness of multilayer 2D materials is a strong function of bending angle, tuning by almost 400% for trilayer graphene [2]. This unusual behavior results from the atomic-scale bending mechanism in 2D multilayers, which is dominated by interlayer shear and slip. In combination with density functional theory (DFT) and continuum mechanics modeling, we derive a unifying model for bending in 2D materials and their heterostructures. Our findings have profound implications on 2D heterostructures, where we demonstrate that the bending stiffness can be controlled by tailoring the interfacial interactions between individual atomic layers of 2D materials.

[1] Lee, C.-H. *et al.* Deep Learning Enabled Strain Mapping of Single-Atom Defects in 2D Transition Metal Dichalcogenides with Sub-picometer Precision. *Nano Lett.* (2020). doi:10.1021/acs.nanolett.0c00269

[2] Han, E. *et al.* Ultrasoft slip-mediated bending in few-layer graphene. *Nat. Mater.*__19__, 305–309 (2020).

2:25pm **LI-WeA1-20 Chemistry in Confined Spaces: 2D-Porous Silicates on Metal Supports*, J. Anibal Boscoboinik,*** Brookhaven National Laboratory **INVITED**

Confinement effects can give rise to interesting properties in the chemistry and physics of small molecules. In this talk, we will explore 2D-porous silicates on a metal support. These can trap noble gases (Ar, Kr, and Xe) at elevated temperatures (>300 K) within the silicate structure and at the interface with the metal. They can also affect chemical reactions taking place on the metal surface, and the case of water formation from H_2 and chemisorbed O will be used to illustrate this effect.

2:45pm **LI-WeA1-24 Basic Science Needs for Transforming Manufacturing Through Atomically Precise Manufacturing*, Cynthia Jenks,*** *H. Lee,* Oak Ridge National Laboratory*; J. Lewis,* Harvard University **INVITED**

In March of 2020, the Department of Energy, Office of Science, Basic Energy Sciences, ran a workshop aimed at providing strategic research directions that could ultimately transform manufacturing as we know it through a better understanding of fundamental science. The attendees at this workshop on Basic Research Needs for Transformative Manufacturing developed five priority research directions to revolutionize manufacturing. These directions include the following: (1) achieve precise, scalable synthesis and processing of atomic-scale building blocks for components and systems; (2) integrate multiscale models and tools to enable adaptive control of manufacturing processes; (3) unravel the fundamentals of manufacturing processes through innovations in operando characterization; (4) direct atom and energy flow to realize sustainable manufacturing; and (5) co-design materials, processes, and products to revolutionize manufacturing. This talk with provide an overview of these five areas with a particular emphasis on the priority research direction on atomically precise manufacturing. Atomically precise materials and molecules would lead to unparalleled structures and functions that, at the moment, are unattainable. There are several scientific questions to consider to achieve precision manufacturing of materials and molecules. W*hat are the mechanisms needed for manufacturing multiscale, atomically and molecularly precise materials? How can basic research uncover structure-function relationships across multiple scales in components and systems? How can chemical processes readily be scaled from laboratory results?*

3:05pm **LI-WeA1-28 Closing Remarks and Thank You's*, Art Utz,*** Tufts University

Thank you for attending today's session! Remember to check out the AVS 67 On Demand Sessions which are available in the mobile app and online scheduler until 11/30/21 and then in the AVS Technical Library for all Platinum Members. We will see you at AVS 68 in Pittsburgh, PA, November 6-11, 2022!

Live Session
Room Live-2 - Session LI-WeA2

Wednesday Afternoon Live Session II: Stop Worrying and Learn to Enable Quantum Science

Moderators: Charles R. Eddy, Jr., Office of Naval Research Global - London, UK, Rachael Myers-Ward, U.S. Naval Research Laboratory

12:50pm **LI-WeA2-1 Welcome and Opening Remarks*, Chip Eddy,*** Office of Naval Research Global - London, UK

Welcome to the AVS 67 Virtual Symposium! We hope you will enjoy the event!

12:55pm **LI-WeA2-2 X-Rays Approaching Neutrons: RIXS with Ultrahigh Resolution and Applied Magnetic Field to Study a Magon-spinon dichotomy in β-Li_2IrO_3*, Alex Frano,*** University of California, San Diego **INVITED**

The family of tri-coordinated iridates have been identified as potential candidates supporting a Kitaev quantum spin liquid, in which spins fractionalize into emergent Majorana fermions and magnetic flux excitations. These quasiparticles acquire long-range topological entanglement and are ideal for fault-tolerant quantum computers. While the presence of additional interactions usually leads to conventional ordering, a dominant Kitaev exchange leads to QSL behavior after the magnetic order is suppressed by temperature or magnetic field, with signatures appearing in thermodynamic measurements and dynamical probes.

β-Li_2IrO_3 is an intriguing example of the complex interplay between Kitaev coupling and magnetic field. At low temperatures, an applied field rapidly suppresses the incommensurate spiral order and drives the system into a uniform field-induced zig-zag state, which are strongly intertwined due to Kitaev interactions. Moreover, a magnetic anomaly has been observed at 100K, with an onset in magnetization and a crossover in the heat capacity without causing true magnetic order. Although these results have been suggested to emerge from thermal fractionalization of the spins, very little is known about the low-energy magnetic excitations.

In this work, we present a comprehensive picture of the dynamical response of β-Li_2IrO_3 in an applied magnetic field. The spin excitations were measured using a high-resolution RIXS spectrometer, which identified dispersing spin waves reaching a maximum of 16meV, in perfect agreement with semiclassical calculations of the dynamical spin structural factor for the intertwined states. The low-energy magnon is superimposed by a broad continuum of excitations centered around 35meV, which is unaffected by the low-temperature ordered states but sensitive to the high temperature anomaly. This continuum is consistent with the onset of nearest neighbor correlations emerging from a dominant Kitaev energy scale, and alludes to the long coherence time of the fractional excitations in the proximate QSL phase.

1:15pm **LI-WeA2-6 X-Ray Spectroscopies With Increased Resolution: Principles and Perspectives*, Lucia Amidani,*** ESRF, France **INVITED**

In was only in the early 90s that the use of hard X-ray emission spectrometers to collect X-ray Absorption spectra was first suggested [1]. X-ray emission spectrometers based on Bragg's law achieve resolutions below 2 eV, a huge improvement compared to solid-state detectors whose resolution is only 150 – 200 eV. With this technical improvement, the characteristic fluorescence of the excited atoms is collected with a resolution below the core-hole lifetime broadening, resulting in better-resolved XAS spectra [2]. Since then, the use of X-ray Spectroscopies with improved resolution exploded and dedicated synchrotron beamlines multiplied. Nowadays, these techniques are largely exploited in many diverse fields of science.

Lanthanides and actinides are among the elements that profit the most of the improved resolution because of their large core-hole lifetime broadenings. Indeed, the demonstration of principle was done on Dy L_3 edge XANES [1]. For actinides, the resolution at L_3 edge is largely improved, but the biggest boost was given to $M_{4,5}$ edges, whose conventional XANES are almost featureless. These edges probe directly the 5f states. With better-resolved spectra, the oxidation state can be easily determined and the spectral features that were invisible before bring information about the local coordination and the charge exchange with ligands [3,4].

The information encrypted in these spectra is enormous. Improved resolution makes it more readily available by disclosing details and allowing smaller differences to be appreciated. However, the interpretation often represent the bottleneck to the extraction of relevant information. In this respect, theoretical simulations are fundamental. Nowadays, we have several user-friendly codes that interprets the spectra starting from different approaches, focusing on the intra-atomic interactions or favouring the multi-atomic picture of the system studied.

In this talk, I will briefly introduce some of the techniques exploiting the improved resolution and then focus on their application to actinide science. I will present few examples illustrating the high potential of these techniques and the approach we use in our group to interpret the data [5–7].

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[1] K. Hämäläinen et al., Phys. Rev. Lett. **67**, 2850 (1991).

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[6] K. O. Kvashnina et al., Angew. Chem. Int. Ed. **58**, 17558 (2019).

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1:35pm **LI-WeA2-10 Exploring Materials, Surface Treatments and Junctions for Superconducting Quantum Circuits***, **Martin Sandberg**,* IBM **INVITED**

Multifunctional material stacks compatible with high coherence superconducting quantum circuits could lead to more efficient circuit implementations. One material with a multitude of applications in optics and electronics is silicon-germanium (SiGe). Here we show that a Si/SiGe heterostructure can be incorporated in superconducting quantum circuits without any coherence degradation [1]. This opens pathways for on-chip optical to microwave transduction among other highly attractive applications.

In addition to the SiGe work we will show the effect of various in-situ surface treatments on flux tunable superconducting qubits in a hermetic package [2], as well as the effect of Two Level Systems (TLSs) in large junction Al/AlOx/Al Merged Element Transmons (MET) [3]. Our studies suggest that surface treatments can reduce the 1/f flux noise without necessarily reducing energy relaxation. For the MET qubits we find that large Al/AlOx/Al junctions contains very strongly coupled TLSs and exhibit large fluctuations in energy relaxation times. Despite the large junction area we still observe energy relaxation times higher than 200 microseconds over several hours of measurements for the best performing devices.

Reference:

[1] Investigating microwave loss of SiGe using superconducting transmon qubits

Martin Sandberg, Vivekananda P. Adiga, Markus Brink, Cihan Kurter, Conal Murray, Marinus Hopstaken, John Bruley, Jason Orcutt, Hanhee Paik

Appl. Phys. Lett. **118**, 124001 (2021)

[2] Effects of surface treatments on flux tunable transmon qubits

M. Mergenthaler,C. Müller, M. Ganzhorn, S. Paredes, P. Müller, G. Salis, V. Adiga,M. Brink,2 M. Sandberg, J. Hertzberg, S. Filipp, and A. Fuhrer

arXiv:2103.07970

[3] Merged-Element Transmons: Design and Qubit Performance

H. J. Mamin, E. Huang, S. Carnevale, C. T. Rettner, N. Arellano, M. H. Sherwood, C. Kurter, B. Trimm, M. Sandberg, R. M. Shelby, M. A. Mueed, B. A. Madon, A. Pushp, M. Steffen, D. Rugar.

arXiv:2103.09163

2:05pm **LI-WeA2-16 Engineering Superconducting Quantum Systems***, J. Yoder, **Donna Ruth Yost**,* MIT Lincoln Laboratory **INVITED**

Development of qubits – the fundamental logic element of a quantum processor – is transitioning from a scientific discovery phase to an engineering pursuit. In order to reach the scale needed for a broad range of quantum computing applications, key challenges now lie in engineering these quantum systems at every level from individual qubits to highly complex circuits. In this talk I will describe our quantum engineering of superconducting qubit systems, including our approach to predictive control of individual qubits and our three-tier stack platform for extending high-coherence circuits to increasing scale and complexity.

This research was funded in part by the Office of the Director of National Intelligence (ODNI), Intelligence Advanced Research Projects Activity (IARPA) and the Defense Advanced Research Projects Agency (DARPA) under Air Force Contract No. FA8702-15-D-0001. The views and conclusions contained herein are those of the authors and should not be interpreted as necessarily representing the official policies or endorsements, either expressed or implied, of the ODNI, IARPA, DARPA, or the U.S. Government.

2:25pm **LI-WeA2-20 Micro-Scale Fusion and Neutron Generation from Nanowire Arrays Irradiated With Ultrashort Laser Pulses of Relativistic Intensity***, **Jorge Rocca**, A. Curtis, C. Calvi,* Colorado State University*; J. Tinsley,* Mission Support and Test Services*; S. Wang, R. Hollinger, H. Song,* Colorado State University*; M. Capeluto,* Colorado State University, USAUniversidad de Buenos Aires, Buenos Aires, Argentina*; Y. Wang, V. Shlyaptsev,* Colorado State University*; V. Kaymak, A. Pukhov,* Heinrich-Heine-Universität Düsseldorf, Germany **INVITED**

The irradiation of arrays of aligned deuterated polyethylene nanowires (CD2) with ultra-high contrast femtosecond laser pulses of relativistic intensity was recently shown to accelerate deuterons to multiMeV energy and to efficiently produce flashes of quasi-monoenergetic fusion neutrons [1]. The trapping of femtosecond laser pulses of relativistic intensity deep within ordered nanowire arrays can volumetrically heat dense matter into a new ultra-hot plasma regime [2,3]. Electron densities more than 100 times greater than the critical density with multi-keV temperatures are achieved using ultrashort laser pulses of only a few Joule energy focused to relativistic intensities. The number of fusion neutron produced exceeds by > 500 times that produced irradiating flat solid CD2 targets with the same laser pulses. Those experiments were conducted at irradiation intensities below 1 x 10 20 W cm-2. We also present recent results of deuteron acceleration from experiments conducted at irradiation intensities of ~ 2 x 10 21 W cm-2. The deuterons are measured to be accelerated to energies of several tens of MeVs and to be emitted in a cone of approximately 10 degrees half-angle. 3-D fully relativistic particle in cell computations are used to elucidate the mechanisms of ions acceleration in the nanowire arrays, which extend beyond target normal sheet acceleration. The fundamental physics of relativistic laser pulse interactions with nanostructures and their promising applications will be reviewed.

Work supported by the Air Force Office of Scientific Research under award number FA9550-17-1-0278 the U.S. Department of Energy, Fusion Science program of the Office of Science using laser facilities of LaserNet US, and MSTS. 1. A. Curtis, et al. , "Micro-scale fusion in dense relativistic nanowire array plasmas". Nature Communications. 9, 1077, (2018). 2. M.A. Purvis, et al., “Relativistic plasma nano-photonics for ultra-high energy density physics,” Nature Photonics 7,796, (2013). 3. C. Bargsten, et al. "Energy Penetration into Arrays of Aligned Nanowires Irradiated with Relativistic Intensities: Scaling to Terabar Pressures," Science Advances, 3, e1601558, (2017)

2:45pm **LI-WeA2-24 The NIST Quantum Logic Clock and its Vacuum Performance***, **David Leibrandt**,* NIST-Boulder **INVITED**

Optical atomic clocks have achieved fractional measurement precision and accuracy at the 10^{-18} level, making them the lowest uncertainty measurement devices of any kind. In this talk, I will describe an optical clock based on quantum-logic spectroscopy of a single Al^+ ion co-trapped with a single Mg^+ ion in an ultra-high vacuum (UHV) environment. Collisions of the ions with background gas molecules degrade the stability of the clock, and cause a systematic frequency shift which must be characterized. By measuring the rate of collisions that cause reordering of the Al^+/Mg^+ ion pair and performing collision kinematics modeling, we determine the background-gas pressure in situ to be 38(19) nPa, where the uncertainty is dominated by the inaccuracy of the semiclassical differential cross sections we use in the model. By incorporating fully quantum scattering calculations, it may be possible to use this pressure measurement technique as the basis of a primary pressure standard for UHV and XHV.

3:05pm **LI-WeA2-28 Closing Remarks and Thank You's***, **Rachael Myers-Ward**,* Naval Research Laboratory

Thank you for attending today's session! Remember to check out the AVS 67 On Demand Sessions which are available in the mobile app and online scheduler until 11/30/21 and then in the AVS Technical Library for all Platinum Members. We will see you at AVS 68 in Pittsburgh, PA, November 6-11, 2022!

2D Materials

Room On Demand - Session 2D-Contributed On Demand

2D Materials Contributed On Demand Session

2D-Contributed On Demand-1 Direct Imaging and Interaction Spectroscopy of Atomic-Scale Ripples on MoS_2 via Atomic Force Microscopy, *O. Dagdeviren,* McGill University, Canada*; O. Acikgoz,* University of California Merced*; P. Grütter,* McGill University, Canada*;* ***Mehmet Z. Baykara,*** University of California Merced

Theory predicts that two-dimensional (2D) materials may only exist in the presence of out-of-plane deformations on atomic length scales, frequently referred to as *ripples*. While such ripples can be detected via electron microscopy, their direct observation via surface-based techniques and characterization in terms of interaction forces and energies remain limited, preventing an unambiguous study of their effect on physicochemical characteristics. Here, we employ high-resolution atomic force microscopy (AFM) to demonstrate the presence of atomic-scale ripples on supported samples of few-layer molybdenum disulfide (MoS_2). Three-dimensional force / energy spectroscopy is utilized to study the effect of ripples on the interaction landscape. Our experiments contribute to the continuing development of a rigorous understanding of the physicochemical characteristics of 2D materials.

2D-Contributed On Demand-4 CVD Growth and Characterization of Ferromagnetic Manganese (IV) Selenide-Epitaxial Graphene Heterostructures, ***Ihteyaz Aqaeed Avash,*** *M. Pedowitz, G. Cassuto, K. Daniels,* University of Maryland, College Park

In recent years, several transition metal dichalcogenides (TMDs) have been found to exhibit intrinsic ferromagnetic properties near the monolayer limit [1,2]. However, manganese diselenide ($MnSe_2$) is of special interest among them since its monolayer 1T polytype has been found to display long-range magnetic ordering and high magnetic moments near room temperature conditions, making it uniquely qualified for various spintronic applications [3,4]. In this study, two-dimensional heterostructure of $MnSe_2$ is grown via Chemical Vapor Deposition (CVD) on few layers epitaxial graphene (EG) synthesized on 6H silicon carbide (SiC) substrate. Two different CVD growth approaches have been investigated in this study: Thermal Vapor Deposition (TVD) and Thermal Vapor Selenification (TVS). In the TVD approach, selenium (Se) powder precursor was used alongside either manganese (IV) oxide (MnO_2) or manganese acetate ($Mn(CH_3CO_2)_2$) powder for direct CVD growth of $MnSe_2$ on epitaxial graphene. In the TVS approach, δ-phase MnO_2 is first electrodeposited on EG using a manganese acetate solution, which is then selenified via CVD using only Se powder precursor.

The samples grown were characterized via Raman, SEM, and AFM tools, all of which demonstrated the presence of $MnSe_2$ growth for both TVD and TVS mechanisms. For both precursor combinations of the TVD approach, the characteristic A_g Raman peak of $MnSe_2$ was visible at 269 cm^{-1}, although its low intensity (almost 40-50% of the control FTA peak of the substrate at 203cm^{-1}) indicates small grain sizes and yield density, a conclusion supported by the SEM and AFM images (around 0.1-0.3µm diameter grains). The yield was found to be slightly higher (about 300% larger grain size) for MnAc compared to MnO_2. For the TVS approach, however, both E_g and A_g peaks were found to be visible (at 145cm^{-1} and 267cm^{-1} respectively) with extremely high peak intensity (around 500% of the control peak), implying significantly higher $MnSe_2$ yield, as also evident in the AFM and SEM data characterized by a high deposition density along the graphene step edges. This comparative study of the two approaches clearly shows TVS to be the far superior mechanism compared to TVD for $MnSe_2$ growth on epitaxial graphene. The TVS approach, once optimized, should result in single-crystal monolayer growth of $MnSe_2$ heterolayer on the epitaxial graphene substrate, potentially leading to the wafer-scale synthesis of $MnSe_2$ based spintronic devices.

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2D-Contributed On Demand-7 Room Temperature Chemical Sensors Based on Molybdenum Disulfide Nanoflower/Epitaxial Graphene Heterostructure, ***Soaram Kim,*** University of Maryland College Park*; J. Park,* Korea Research Institute of Standards and Science, Korea (Republic of)*; M. Pedwitz, D. Lewis,* University of Maryland College Park*; S. Lee,* The Ohio State University*; B. Uppalapati, D. Khan, F. Bayram, G. Koley,* Clemson University*; S. Kang,* Korea Research Institute of Standards and Science, Korea (Republic of)*; K. Daniels,* University of Maryland College Park

In recent years, a van der Waals heterostructure device, stacking 2D architectures atomically with synergistic combinations of nanomaterials have attracted tremendous attention with many potential applications such as chemical sensors in environmental and safety monitoring, and medical diagnostics and biomedical health care systems [1,2]. Atomically thin 2D graphene and transition metal dichalcogenides (TMDs) have an extremely high surface-to-volume ratio which is the most critical parameter for chemical sensing applications. Here we have fabricated a heterostructure of molybdenum disulfide (MoS_2) nanoflower and epitaxial graphene on 6H silicon carbide (SiC) substrate for chemical sensing. We have combined the advantages of high sensitivity and fast response time of graphene with the high surface-to-volume ratio of MoS_2 nanoflower to develop a room temperature chemical sensor for health/environmental monitoring systems.

Bilayer epitaxial graphene (EG) was synthesized by Si sublimation on 6H SiC, and MoS_2nanoflowers were grown on graphene/SiC directly using metal-organic chemical vapor deposition (MOCVD). The growth methods of graphene and MoS_2 nanoflowers are discussed in detail elsewhere [3,4]. The structural and optical properties of the samples were investigated by scanning electron microscopy (SEM), atomic force microscope (AFM), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, photoluminescence (PL), and cyclic voltammetry (CV). To fabricate the chemical sensor, e-beam lithography and reactive ion etching (RIE, CF_4) were used to prepare a simple pattern. Finally, the metal electrode (Ti/Au = 30/120 nm) was deposited using an e-beam evaporator. The prepared chemical sensor was tested with various gases such as 5 ppm of nitrogen dioxide (NO_2) and ammonia (NH_3), and ~1000 ppm of volatile organic compounds (VOCs) and showed a superior chemical response and recovery at room temperature. It is evident that the prepared device is suitable for chemical sensing applications such as health and environmental monitoring systems.

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2D-Contributed On Demand-10 Structural Characterization of Cobalt Sulfide Sheets Supported on Au(111), ***Mahesh Krishna Prabhu****, I. Groot,* Leiden University, Netherlands

Transition metal dichalcogenides (TMDCs) are a type of 2D materials widely investigated by both experimentalists and theoreticians, because of their unique properties.In the case of cobalt sulfide, density functional theory (DFT) calculations on freestanding S-Co-S sheets suggest there are no stable 2D cobalt sulfide polymorphs, whereas experimental observations clearly show TMDC-like structures on Au(111). In this study we resolve this disagreement by using a combination of experimental techniques and DFT calculations, considering the substrate explicitly. We find a 2D CoS(0001)-like sheet on Au(111) that delivers excellent agreement between theory and experiment.Uniquely this sheet exhibits a metallic character, contrary to most TMDCs, and exists due to the stabilizing interactions with the Au(111) substrate.

2D-Contributed On Demand-13 Edge Channels of Broken Symmetry Quantum Hall States in Graphene probed by Atomic Force Microscopy, ***Sungmin Kim,*** *J. Schwenk,* National Institute of Standards and Technology (NIST)/ University of Maryland, College Park*; D. Walkup,* National Institute for Science and Technology (NIST)*; Y. Zeng,* Columbia University*; F. Ghahari,* National Institute of Standards and Technology (NIST)/ University of Maryland, College Park*; S. Le,* National Institute of Standards and Technology (NIST)*; M. Slot,* National Institute for Science and Technology (NIST)*; J. Berwanger,* University of Regensburg, Germany*; S. Blankenship,* National Institute for Science and Technology (NIST)*; F. Giessibl,* University of Regensburg, Germany*; N. Zhitenev,* National Institute for Science and Technology (NIST)*; C. Dean,* Columbia University*; J. Stroscio,* National Institute for Science and Technology (NIST)

The quantum Hall (QH) effect, a topologically non-trivial quantum phase has brought into focus the concept of topological order in physics. The topologically protected quantum Hall edge states are the essential features of the QH effect, however microscopic local probe studies of edge state have been limited. The QH edge states in graphene are special since they emerge from four-fold nearly-degenerate Landau levels. In this talk, we present a microscopic study a of the QH edge states originating from the broken symmetry zero Landau level (zLL) in graphene. The edge states emerging from integer filling factors of v = 0, ±1 are spatially mapped across the quantum Hall edge boundary using atomic force microscopy (AFM) and Kelvin probe force microscopy (KPFM) technique. The measurements of chemical potential within the four-fold degenerate zLL suggest a change in the microscopic spin/valley ordering as a function of magnetic field caused by the interplay of the moiré superlattice potential of the graphene/hBN system and other symmetry breaking effects.

2D-Contributed On Demand-16 Band Gap Tuning in Lateral Heterostructures of Mose$_{2(1\text{-}x)}$S$_{2x}$-Wse$_{2(1\text{-}x)}$S$_{2x}$ TErnary Alloys*, Florence Ann Nugera, P. Sahoo,* University of South Florida*; Y. Xin,* National High Magnetic Field Laboratory, Florida State University*; H. Gutierrez,* University of South Florida

Transition metal dichalcogenides (TMDs) ternary alloys have composition dependent electronic properties, such as bandgap, work function, and electrical response (n-type or p-type conductivity). When individual ternary alloys are combined to form heterostructures, their functionality can be greatly expanded compared to heterostructures based on binary alloys. Thus, opening a path for new optoelectrical applications with flexible designs and enhanced properties. In this work, we successfully synthesize lateral heterostructures with monolayer, bilayer and trilayer thicknesses based on ternary alloys of the type MoSe$_{2(1\text{-}x)}$S$_{2x}$-WSe$_{2(1\text{-}x)}$S$_{2x}$, where x is the chalcogen atom composition. The continuous tuning of the band gap for both materials, is demonstrated. The composition homogeneity of each domain was studied by photoluminescence (PL) and Raman spectroscopy, while Kelvin probe force microscopy (KPFM) was used to study the tunable band alignment at the heterojunctions.

2D-Contributed On Demand-19 Nonuniform Debye Temperatures in Quasi-One-Dimensional TiS$_3$ and ZrS$_3$*, Archit Dhingra, P. Dowben,* University of Nebraska-Lincoln, USA

TiS$_3$ and ZrS$_3$ are quasi-one-dimensional n-type van der Waals semiconductors that offer an opportunity to fabricate transistors with widths < 10 nm, as they lack undesirable edge effects unlike other well-studied two-dimensional materials (namely: graphene and transition metal dichalcogenides). TiS$_3$ and ZrS$_3$ have modest band gaps of ~1 eV and ~1.8–2.1 eV, respectively, and both the materials are highly anisotropic. The combination of adequate band gaps and appreciable electron mobilities indicates some potential for these metal trichalcogenides materials in applications in beyond CMOS sensor electronics. Temperature dependent x-ray photoemission spectroscopy (XPS) measurements were employed to obtain a quantitative picture of electron-phonon scattering in these materials. The Debye–Waller factor plots for S 2p core-level of TiS$_3$, based on the temperature dependent XPS measurements, hint that effective Debye temperatures of the two different kinds of sulfur coordination are 464 ± 35 K and 547 ± 26 K. Whereas the Debye–Waller factor plots for the S 2p core-level of ZrS$_3$ suggest effective Debye temperatures of 558 ± 30 K and 667 ± 35 K for, again, the two different sulfur coordination. The apparent difference between the effective Debye temperatures of different sulfurs, within the material, is an expected consequence of dissimilar coordination number. Additionally, the high effective Debye temperatures of the different sulfur species in ZrS$_3$ than in TiS$_3$ imply that the trichalcogenide of zirconium is stiffer than its titanium counterpart, which translates to reduced electron-phonon scattering in the former. This conclusion is further supported by the temperature dependent filed-effect mobility measurements, which consistently indicate that the carrier mobility of ZrS$_3$ is less sensitive to temperature changes in comparison with that of TiS$_3$. Even though the electron-phonon scattering is implicated as the cause for the much lower measured mobilities compared to the predicted high carrier mobilities (~10,000 $cm^2V^{-1}s^{-1}$ for TiS$_3$ and ~1,800–2,500 $cm^2V^{-1}s^{-1}$ for ZrS$_3$), the relatively high Debye temperatures indicate that there are only a limited number of soft phonon modes for these materials, which can be possibly suppressed, leading to improved mobilities.

2D-Contributed On Demand-22 3D Spin Polarized – Angle Resolved Photoemission Spectroscopy (SP-ARPES) setup at IMDEA Nanociencia*, **Beatriz Muñiz Cano**, M. Valbuena Martinez,* IMDEA Nanociencia, Spain

Angle-Resolved Photoemission Spectroscopy (ARPES) is a fundamental tool to visualize the momentum-dependent electronic bands of materials, revealing relevant characteristics, parameters and new interactions [1, 2] in them. Spin-ARPES (SR-ARPES) adds up spin resolution and, by measuring spin polarization, allows the complete determination of a quantum state [3]. The SRARPES technique has been proven to be extremely powerful in recent years as it allows studying spin-polarized electronic states in two-dimensional (2D) systems with strong spin-orbit coupling

(SOC), whose related phenomena, such as the Rashba effect or the appearance of topological insulators (TI), give rise to new interactions and particularly relevant electronic states, which can be exploited in spintronics and spin-orbitronics [4]. In this sense, interfacing Rashba or topological surface electronic states with ferromagnetic thin films (FM/SOC) [5, 6] can modify their spin texture and be at the origin of emerging phenomena as spin-charge conversion, switching out-of-plane magnetization by spin transfer-torque, DM Interaction and chiral spin structures as skyrimions, or the

quantum anomalous Hall Effect [7]. Thus, controlling interfacial interactions and their effect on spin-polarized electronic states is crucial. In this contribution we will present the new SR-ARPES facility at IMDEA Nanoscience which includes a 3D mini-Mott Spin Detector, which allows the determination of the 3D spin components (two in-plane and one out-of-plane). So far, we have measured the Rashba surface state spin texture in Au(111) (Fig. 1), including Fermi surface (FS) mapping and spin resolved measurements in valence band (VB) and surface state (SS). Finally, some perspectives for the study of 2D topological quantum materials or emerging phenomena in FM/SOC interfaces will be presented as well as some experiments related to the abovementioned phenomena arising from SOC and that, in the light of previous results obtained in the group, are expected to be continued with this new system and further developed in different synchrotron facilities.

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2D-Contributed On Demand-25 Tuning Ferromagnetic Properties of Monolayer CrI$_3$ via Molecular Adsorption*, **Jiho Yang**, B. Shong,* Hongik University, Korea (Republic of)

Two-dimensional (2D) materials with various electrical and optical properties are attracting large research interests. Moreover, ferromagnetic(FM) 2D materials possess interesting possible applications such as sensors and data storage. For example, CrI$_3$ has been shown to exhibit FM properties as either bulk or monolayer structures. However, its relatively low Curie temperature of ca. 45K hinders device application of CrI$_3$. In this work, we employ density functional theory (DFT) calculations with spin orbit coupling (SOC) to examine the adsorption of NH$_3$, PH$_3$, NO and NO$_2$ on 2D monolayer CrI$_3$. The variations in the adsorption energy and charge transfer, and the resulting changes in the band structure and the magnetic anisotropy are analyzed. In addition, the shifts in the Curie temperature according to the molecular adsorption are estimated via Monte Carlo simulations assuming Ising model.

2D-Contributed On Demand-28 Electron Emission from Quasi-freestanding Bilayer Epitaxial Graphene Microstructures*, **Daniel Lewis**, K. Daniels,* University of Maryland, College Park

Graphene microstructures have been shown to exhibit controllable directional electron emission when carrying a current under an accelerating electric field. Through Phonon-Assisted Electron Emission (PAEE), graphene microstructures demonstrate electron emission at electric field intensities and lattice temperatures below what would be expected for carbon to demonstrate field emission or thermionic emission, respectively. Furthermore, such emissions tend to be out of the plane of the graphene microstructure, allowing control of the directionality of the emission current even before being directed with an applied electric field.

Thus far, such arrangements have tended to involve structural dimensions in the range of micrometers, commonly with CVD-transferred graphene and carbon nanotubes. However, even with hundreds of kV/cm applied fields, emission currents rarely exceed a few nA. Herein are examples of the characteristics and tunable variables demonstrated by multiple epitaxial graphene structures, with dimensions up to cm, capable of producing >1 µA emission currents in applied fields of 2 kV/cm.

Quasi-freestanding epitaxial graphene on a silicon carbide substrate offers several advantages compared to transferred graphene or unzipped nanotubes, including lower defect density, greater structural integrity, ease of handling, and compatibility with simple photolithography fabrication techniques. The devices presented here were fabricated with a low-cost, wafer scalable, single-photomask process that obviates the need for material transfer to a second substrate and is easily tailored to create any variation in design parameters.

Initial tests demonstrate clear patterns of behavior in device performance linked to multiple testable variables, including device and substrate temperature, input power, applied field, dimensions, morphology and orientation, and cycle time. Results presented here show these influences affecting device output by up to an order of magnitude in some cases, while investigations of device durability and operational lifetime are ongoing. These graphene microstructure electron sources may provide a means for device implementation in a 2D heterostructure environment or as a vehicle for further miniaturization of constructs requiring controllable electron emissions, such as electron microscopy or X-ray generation.

2D-Contributed On Demand-31 From Energy Dissipation on Dirac Materials to Intermediate Stages of Hexagonal Boron Nitride Growth*,* ***Anton Tamtögl****, A. Ruckhofer,* Graz University of Technology, Austria*; N. Avidor,* University of Cambridge, UK*; M. Sacchi,* University of Surrey, UK*; M. Bremholm, P. Hofmann,* Aarhus University, Denmark*; G. Benedek,* University of Milano-Bicocca, Italy*; W. Allison,* University of Cambridge, UK

We have been studying various processes of energy dissipation in order to understand the nanoscale surface dynamics of Dirac materials experimentally and theoretically. Among this material class, topological insulators such as Bi_2Te_3 exhibit an insulating gap in the bulk while the surface is electrically conducting [1]. However, in real samples and at finite temperatures, their ideal zero-Kelvin behaviour is perturbed and scattering processes via electron-phonon (e-ph) coupling can give rise to energy losses. In this context atom-surface scattering has been demonstrated to be a sensitive probe to determine the surface phonon dispersion and the e-ph interaction parameter [1-3]. We will discuss the influence of the dimensionality on the e-ph coupling [4], when considering low-dimensional or quasi one-dimensional systems [5].

Furthermore, the lineshape broadening upon inelastic scattering from surfaces can be used to determine the characteristics of energy dissipation upon the motion of atoms and molecules [6,7]. Using this technique, we have studied the diffusion of water on the surfaces of Dirac materials (graphene and the topological insulator Bi_2Te_3)[7].Thus, we can specify the mechanisms underlying the motion of water and, by comparison with first-principle calculations, we identify aspects of its adsorption geometry, as well as the energy landscape for the motion. We see clear evidence for repulsive interactions between water molecules, which is contrary to the expectation that attractive interactions dominate the behaviour and aggregation of water. We are also able to make a qualitative assessment of the rates of energy transfer between water molecules and the topological insulator on which they move.[7].

Finally, we will discuss some recent experimental findings about the growth of hexagonal boron nitride (hBN) on Ru(0001). The growth of hBN on metal substrates, based on chemical vapour deposition, is well documented in literature [8]. In contrast to the reported structure of hBN after following the“ideal” growth conditions, we observe several intermediate structures, prior/parallel to the hBN growth, which, depending on the experimental conditions, can be transferred into each other or hBN.

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2D-Contributed On Demand-34 Observation of Intra-Unit-Cell Nematic Order in Epitaxial Bilayer FeSe Films on $SrTiO_3$(001)*,* ***Lian Li****, H. Zhang,* West Virginia University, USA*; M. Weinert,* University of Wisconsin, Milwaukee

Epitaxial FeSe thin films provide an ideal platform to probe the interplay of superconductivity and nematicity, due to the absence of long-range magnetic order. Here, we systematically investigate the nematic order in high quality bilayer FeSe/$SrTiO_3$ films grown by molecular beam epitaxy.Using low temperature scanning tunneling microscopy/spectroscopy, we observe features associated with Se atoms to be elongated along the Fe-Fe lattice direction within a specific energy window, demonstrating symmetry breaking from fourfold to twofold. Detailed analysis of Fourier transformation of the STM images reveals that the intensity of Fe Bragg peak breaks rotational symmetry within each Fe unit cell, indicative of an intra-unit-cell nematicity.Our results provide critical information on nematicity in Fe-based superconductors, an essential element in understanding superconducting transition in these materials.

This research is supported by DOE (DE-SC0017632).

2D-Contributed On Demand-37 Phase Dependent-Nanoscale Friction on Two Dimensional Layers*,* ***Dooho Lee****, H. Lee, J. Park,* Korea Advanced Institute of Science and Technology (KAIST) & Institute for Basic Science (IBS), Korea (Republic of)

Molybdenum disulfide (MoS_2) is one of the transition metal dichalcogenides (TMDs), having a layered structure like graphene. The monolayer of MoS_2 is an atomically thin semiconductor with a bandgap of 1.8 eV, which makes it good potential applications in nanoelectronics, optoelectronics, and sensors. Unlike graphene, which takes a significant portion in the studies about two-dimensional (2D) material, MoS_2 has many crystalline structures. Nanotribological study about the phase dependence will provide an important fundamental understanding of MoS_2, as well as TMDs.

In this contribution, we turned mechanically exfoliated 2H-MoS_2 into 1T-MoS_2 by lithiation process. We measured atomic-scale tribological and electrical properties of MoS_2 including friction, with atomic force microscopy (AFM). We report that with the phase transition of 2H to 1T, the friction of MoS_2 monolayer has greatly increased. We show that friction proportion of 2H-MoS_2 and 1T-MoS_2 is 0.19 : 1.1, with normalization to the value of mica. We attribute the friction increase of 1T-MoS_2 with increased overlap of phonon density of states (DOS) with mica substrate.

We also measured friction of $MoTe_2$, of which the pure 1T phase is commercially available since it shows stable 1T phase, as well as 2H phase. Friction proportion of exfoliated 1T-$MoTe_2$ and 2H-$MoTe_2$ is 0.12 : 1.07, normalized with the friction of mica. This study gives insight to the universal trend of the phase-dependent tribological effects on two-dimensional atomic layers.

2D-Contributed On Demand-40 A Full Gap Above the Fermi Level: The Charge Density Wave of Monolayer VS_2*, C. van Efferen,* II. Physikalisches Institut, University of Cologne, Germany*; J. Berges,* Institut für Theoretische Physik, University Bremen, Germany*; J. Hall,* II. Physikalisches Institut, University of Cologne , Germany*; E. van Loon,* Institut für Theoretische Physik, University Bremen, Germany*; S. Kraus,* II. Physikalisches Institut, University of Cologne, Germany*; A. Schobert,* Institut für Theoretische Physik, University Bremen, Germany*; T. Wekking, F. Huttmann, E. Plaar,* II. Physikalisches Institut, University of Cologne, Germany*; N. Rothenbach,* Fakultät für Physik und Center für Nanointegration, University Duisburg-Essen, Germany*; K. Ollefs,* Fakultät für Physik und Center für Nanointegration, University Duisburg Essen, Germany*; L. Machado-Arruda,* Institut für Experimentalphysik, FU Berlin, Germany*; N. Brookes,* European Synchrotron Research Facility, France*; G. Schönhoff,* Institut für Theoretische Physik, University Bremen, Germany*; K. Kummer,* European Synchrotron Research Facility, France*; H. Wende,* Fakultät für Physik und Center für Nanointegration, University Duisburg-Essen, Germany*; T. Wehling,* Institut für Theoretische Physik, University Bremen, Germany*;* ***Thomas Michely****,* II. Physikalisches Institut, University of Cologne, Germany

In the weak-coupling Peierls' view, charge density wave (CDW) transitions are metal-insulator transitions, creating a gap at the Fermi level. However, with strong electron-phonon coupling, theoretically the effects of the periodic lattice distortion could be spread throughout the electronic structure and give rise to CDW gaps away from the Fermi level. Here, using scanning tunneling microscopy and spectroscopy, we present experimental evidence of a full CDW gap residing in the unoccupied states of monolayer VS2. Our ab initio calculations show anharmonic coupling of transverse and longitudinal phonons to be essential for the formation of the CDW and the full gap above the Fermi level. The CDW induces a Lifshitz transition, i.e., a topological metal-metal instead of a Peierls metal-insulator transition. Additionally, x-ray magnetic circular dichroism reveals the absence of net magnetization in this phase, pointing to a coupled CDW-antiferromagnetic ground state.

2D-Contributed On Demand-43 Ferroelectrics Meet Ionics in the Land of van der Waals*, **Petro Maksymovych**, S. Neumayer,* Oak Ridge National Laboratory*; A. Ohara, S. Pantelides,* Vanderbilt University*; N. Balke,* Oak Ridge National Laboratory

Ionic conductivity is often considered a limiting factor for polarization switching or even incompatible with ordered ferroelectric states. Indeed, ionic conduction breaks down the dielectric state and gives rise to disorder, both of which should be detrimental for ferroelectricity. Recently we carried out comprehensive analysis of $CuInP_2S_6$ [1] – a lesser known ferroelectric material that represents a broad family of chalcogenophosphate van der Waals crystals. The polarization in this material is mainly governed by the displacement of Cu ions, which is also the most mobile ionic species. In this talk we will show that the van der Waals structure of this material combined with the high intrinsic mobility of Cu enables the intersection of ionic and ferroelectric properties, and gives rise to a rich spectrum of intriguing properties rare or even non-existent in known ferroelectric and ionic conductor materials.

The very large (by standards of ferroelectricity) displacement can be viewed as incipience of ionic conductivity. Density functional theory calculations and piezoresponse force microscopy have revealed that owing to such displacements, four distinct uniaxial polarization states arise in $CuInP_2S_6$ [2], including a previously unknown state that doubles spontaneous polarization. The resulting highly anharmonic potential for Cu motion in the ferroelectric state furthermore enables giant negative electrostriction, and a free energy potential highly susceptible to strain. Electric fields can also activate ionic currents [3], even in the ferroelectric state. Through a careful analysis of piezoelectric imaging data, we have concluded that activating ionic conduction by above-threshold fields unexpectedly switches polarization orientation inside the film. This ionically mediated mechanism is fundamentally different from dipole rotation that is typically expected for ferroelectrics. This symbiotic interplay of ferroelectric and ionic phenomena enables new approaches to control polarization. Moreover, it inspires a change in perspective on nucleation, domain wall dynamics and other ferroelectric characteristics in material systems where ionic and ferroelectric phenomena manifest.

The experimental work were supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, Materials Science and Engineering Division. The experiments were conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility. Theoretical work at Vanderbilt University was supported by Department of Energy grant DE-FG02-09ER46554 and by the McMinn Endowment.

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2D-Contributed On Demand-46 Multicomponent Monolayer Manipulation Through Successive Ultraviolet Irradiation*, **Cynthia Gerber**,* University of Connecticut

Mixed self-assembled monolayers can be manipulated to potentially control surface functionality through the facilitation of multi-molecule organization. The incorporation of anthracene dicarboxylic acid (AnDCA) in the monolayer causes greater disorder in the octanethiol domains. In this study, we analyzed the effects of ultraviolet radiation on a mixed monolayer of octanethiol and anthracene dicarboxylic acid. The UV radiation was sequentially applied in 10 minute increments and imaged by scanning tunneling microscopy after each round. The initial doses of UV light caused the octanethiol domains to diminish and further doses caused the octanethiol to reconstruct in striped phases with separate ordered domains of hydrogen-bonded AnDCA. This research contributes to the understanding of how exposure to ultraviolet light affects multicomponent monolayer construction of ordered domains and phase changes.

2D-Contributed On Demand-49 Thermally Induced Complex Reactions Pathways between Ws_2 and Au-Ti Substrates*, A. Costine ,* University of Virginia, USA*; J. Fonseca Vega, J. Robinson, C. Cress,* Naval Research Laboratory, USA*; **Petra Reinke**,* University of Virginia, USA

The fabrication of transistors which make use of the unique and versatile properties of transition metal dichalcogenides requires development of enabling technology for integration. This includes contacts, packaging, and stacking of electronically functional components. Ti-Au layers are common in transistor design and function as adhesion layer (Ti) and contact (Au). In our work the WS_2 flakes are transferred onto the Au-surface using micromechanical cleavage with a common adhesive, and subsequently integrated in a device structure. We probed the thermal stability of the Ti-Au-WS_2 stack by combining in-situ annealing with XPS analysis with small temperature intervals of 10-30°C in the temperature range from 200° to 625°C. The WS_2 layer itself is surprisingly stable with the onset of S-loss around 350°C, which is followed by formation of W-carbide and oxide (reaction with residue), and reduction to W(0) above 550°C. At the same time the Au-contact undergoes a dramatic change, and alloying with Ti occurs through rapid diffusive processes starting at 250°C, and concomitant reaction of surface Ti to form Ti-carbide and oxides through reaction with the residue from the TMD transfer. Ti-S compounds emerge only above 500°C. Alloying is suppressed if the Ti can rapidly react with surface carbon, oxygen and Ti diffusion is therefore transient limiting the formation of an alloy. However, if the concentration of the residue is low or a high coverage with WS_2 is achieved, the Ti-carbide and oxide formation is limited and Au-Ti alloys dominate. This reaction sequence leads to modification of the contact and can contribute to erratic, or irreproducible device performance. We will discuss the reaction pathways in detail, and use samples with and without WS_2, which acts as a control, and for different annealing conditions which interrupt Ti diffusion, to support our interpretation. The temperature induced modulation of the Au-TMD interface will degrade device performance, and requires to adapt the current strategies for device integration.

2D-Contributed On Demand-52 The (Mostly) Unwelcome Guest in 2D Chalcogenides: Native oxidation rates and the effects of oxygen during processing MoS_2, TiS_2, and $Zr(S,Se)_2$*, **Rafael Jaramillo**,* Massachusetts Institute of Technology

Being a very hard anion, oxygen bonds very differently to transition metals than do the chalcogens. Trace oxygen in a transition metal dichalcogenide (TMD) has a substantial impact on material processing and properties, much more so than for instance trace selenium in a sulfide. Since oxygen is all around us, even in our high-vacuum chambers, it is essential to understand and control the effects of oxygen on processing 2D materials. We report the results of three studies of the effect of oxygen on processing TMDs. We find that lowering trace oxygen concentration in the reactor makes it possible to lower the processing temperature for large-area TiS_2 films, made by reacting Ti thin films with H_2S gas. We quantify how lowering oxygen concentration enables faster metal sulfurization at lower temperatures (down to 500°C), leading to thin films that are smooth and homogeneous. In contrast, we find the opposite trend for MoS_2: *adding* trace oxygen enables lower processing temperatures (down to 375°C) for large-area MoS_2 films, made by sulfurizing Mo thin films. We understand these contrasting effects in the light of particulars of Ti-O and Mo-O bonds, including molecular dynamics (MD) simulations that suggest that oxygen is a catalyst for Mo-S bond formation. We also report a quantitative study of the rate of oxidation of freshly-cleaved surfaces of MoS_2 and $Zr(S,Se)_2$. MoS_2 surfaces remain pristine for over a year in laboratory ambient conditions, without a trace of oxide formation. In contrast, $Zr(S,Se)_2$ alloys oxidize rapidly, with the native oxide growing at a rate up to 0.5 Å/min. MD simulations reveal the kinetic mechanisms that limit native oxide growth for MoS_2 and promote it for $Zr(S,Se)_2$, despite oxide formation in ambient conditions being thermodynamically-favorable in all cases.

2D-Contributed On Demand-55 Correlative Analysis Strategies for Transition Metal Dichalcogenides*, **Umberto Celano**,* IMEC, Belgium

Considering their widespread use in future electronics and photonic applications, 2D materials are attracting the attention of the metrology community.[1] Considered an exciting class of 2D materials, transition metal dichalcogenides (TMDs) can be used to build devices whose optoelectronic properties are strongly influenced by the intrinsic and extrinsic defects, growth and transfer methods involved in their fabrication. Furthermore, considering complex integration schemes and stacked TMDs heterostructures, the detailed comprehension of the interaction of defects between layers and the capability to sense them have an even higher importance.[2]Therefore, it is crucial to develop metrology solutions to interpret defects-related phenomena on the nanometer scale for TMDs, and this remains a challenge for the community. Notwithstanding the complexity, the well know flexibility of atomic force microscopy (AFM) offer multiple alternatives for sensing TMDs properties in individual layers and heterostructures. For example, using electrical and electrostatic tip-sample interactions, as in conductive atomic force microscopy (C-AFM) and Kelvin probe force microscopy (KPFM), various atomic-scale defects can be identified and characterized.[3] Similarly, near-field methods such as tip-enhanced Raman spectroscopy (TERS) and compositional techniques such as secondary ions mass spectroscopy (SIMS), can team up to obtain the direct correlation between growing substrates and TMDs films quality. Here, using these and other techniques, we present a metrological analysis scheme that allow the (averaged) electrical characteristics of TMDs-devices to be correlated to the local material properties for a deeper connection to device physics.

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2D-Contributed On Demand-58 Measuring Van der Waals Interactions of Monolayer Materials*, Stanislav Tsoi,* US Naval Research Laboratory*; S. Sivaram,* Sila Nanotechnologies Inc.*; M. Rosenberger,* University of Notre Dame*; K. McCreary,* US Naval Research Laboratory*; H. Chuang,* Nova Research*; B. Jonker,* US Naval Research Laboratory

Van der Waals interactions play a major role in the science of monolayer materials, yet their measurement has received a limited attention. We exploit AFM to measure an attractive van der Waals (vdW) force acting on a sharp AFM tip from a composite sample consisting of a monolayer material supported on a thick substrate. The force is measured as a function of a separation between the tip and the monolayer/substrate stack in the range from 2-20 nm for graphene/silicon oxide, fluorinated graphene/silicon oxide, MoS_2/graphite and $MoSe_2$/graphite. The obtained results indicate that distinct contributions to the force from the monolayer and substrate can be distinguished by their different dependence on the separation, an inverse cubed for the former and inverse square for the latter. Thus, van der Waals interaction for different monolayer materials is determined and compared to the traditional bulk materials. Further, we demonstrate that the monolayer materials screen van der Waals interactions of the underlying substrate, with full screening in graphene/silicon oxide and partial screening in fluorinated graphene/silicon oxide, MoS_2/graphite and $MoSe_2$/graphite.

2D-Contributed On Demand-61 Measuring Surface Phonon Dispersion*, Timo Watjen,* Scienta Omicron, Sweden

Many interesting material properties cannot be described without a many body electronic structure approach. Electrons may interact not just with other electrons but also couple to bosons, for instance by electron-phonon coupling (EPC). ARPES measurements have revealed ‘kinks’ in the electron dispersion curves and EPC has been discussed as one possible origin [1-4]. This interaction highlights the need of phonon dispersion data which today largely relies on simulations. An experimental technique to access surface phonon dispersion is high resolution electron energy loss spectroscopy (HREELS). Traditionally, HREELS involved mechanically rotating the setup probing one angle and energy channel at the time. Operating such a setup is time consuming and has limited angular resolution. Here, we present a HREELS solution with monochromatic collimated electron source and a hemispherical analyzer [5]. The 2D detector of the analyzer, which simultaneously spans hundreds of channels in both the energy and angular directions, enables a massive speed-up in data collection. While ARPES enables electron dispersion measurements, HREELS can complement these with surface phonon dispersion curves in the same instrument.

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2D-Contributed On Demand-64 Two Dimensional TMDs Based Thermo-Electric Devices for Energy Harvesting from Waste Heat*, Sangram Pradhan,* *M. Mbaye, M. Behera, M. Bahoura,* Norfolk State University

High conformal with large area transition metal dichalcogenides (TMDs) crystalline thin films were grown at optimum substrate temperature using physical vapor deposition. Fundamental films properties were investigated using Structural, morphological and electrical techniques. XRD data revealed that TMDs (MoS_2 and WS_2) films are highly crystalline in nature and oriented in 00l plane. Thermal conductivity behavior of MoS_2 film also shows low value at room temperature which is excellent to achieve higher thermoelectric figure of merit close to 2. Raman spectroscopy data shows two distinct MoS_2 vibrational modes corresponding to signature E^1_{2g} and A^1_g peak of TMDs. Electrical, thermoelectric transport studies further demonstrated that MoS_2 films show p-type thermoelectric characteristics, while WS_2 is an n-type material. Finally, highly-efficient thermal energy harvesting pn-junction based thermoelectric generator were fabricate out of these TMDs for waste heat recovery and converted to electrical energy.

2D-Contributed On Demand-67 Behind the Scenes of Electron Induced Deposition of Amorphous-BN_x on Graphene - A Surface Science Study*, Virginia Boix,* Lund University, Sweden*; C. Struzzi,* MaxIV laboratory, Sweden*; T. Gallo, N. Johansson, G. D'Acunto, Z. Yong,* Lund University, Sweden*; A. Zakharov,* MaxIV laboratory, Sweden*; Z. Li,* Aarhus University, Denmark*; J. Schnadt, A. Mikkelsen, J. Knudsen,* Lund University, Sweden

A necessary tool for reducing the environmental impact of electronic devices is developing higher-performance and more energy-efficient components. Stacked heterostructure devices of two-dimensional (2D) materials are emerging as promising building blocks for such applications [1]. In such devices, conductive, semiconductive, and dielectric 2D materials are combined to reach the desired electrical function. The most used dielectric in 2D applications is hexagonal boron nitride (h-BN). However, direct synthesis of h-BN on top of 2D materials is complex due to their inert nature and the low growth temperature requirements for stacked electronics.

An exciting solution for these manufacturing constraints is to substitute the crystalline 2D h-BN with a thin film of amorphous-BN (a-BN) [2]. It has been recently reported that ultrathin films of a-BN have a bandgap similar to their crystalline counterpart and retain much of the valued chemical inertness and high thermal stability of h-BN [3]. Moreover, a-BN can be easily manufactured with high spatial resolution and low-temperature processing using Focused Electron Beam Induced Deposition (FEIBD) [4]. However, even though FEIBD is a widely used method [5], a thorough understanding of the electron assisted deposition, where multiple simultaneous processes compete with each other, is lacking.

In this contribution, we report on our surface science study of electron beam-induced deposition of amorphous-BN_x on graphene at room temperature [6]. Using a combination of X-ray Photoelectron Spectroscopy, Low Energy Electron Microscopy, and Scanning Tunneling Microscopy, we identify the essential steps of the deposition process, which highly influence the morphology of the heterostructure, its chemical composition, and its interaction with the substrate. We reveal a much higher decomposition of the precursor molecule than previously thought and a strong interaction with the substrate, which does not affect the structural integrity of the graphene. These results help explain the high boron concentration usually found in FEBID BN films and the thermal stability of the resulting structure.

Our studies provide a valuable surface science insight into using electron beams to synthesize stable and inert layers in 2D heterostructures. Moreover, we aim to spark a discussion about further applications of FEBID, such as confined doping and functionalization of graphene (or other 2D films), patterned adsorption of mass-selected ions, or patterning of adsorbates as anchors for attaching bigger molecules.

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2D-Contributed On Demand-70 Formation, Structure and Properties of 2D Silica and Transition Metal Silicates on Gold*, N. Doudin, K. Saritas, S. Ismail-Beigi,* ***Eric Altman,*** Yale University

Two-dimensional silica has attracted attention as model catalysts, ultimate permeation membranes, while related 2D transition metal silicates have potentially interesting piezoelectric and magnetic properties. Gold's inert, non-magnetic nature makes it an attractive substrate for model catalyst studies and investigation of 2D magnetic layers. Here we report on experimental and theoretical studies on the growth and structure of 2D silica and transition metal silicates on polycrystalline Au and Au(111). Experimental reflection absorption infrared spectroscopy, electron diffraction and scanning tunneling microscopy (STM) indicate that 2D silica bilayers can be formed by both atomic layer deposition and molecular beam epitaxy. By adjusting the imaging bias, it was possible to peer through the insulating 2D silica to image the underlying Au surface which revealed that the Au(111) herringbone reconstruction was scarcely affected by the 2D silica bilayer, consistent with the expected weak van der Waals interaction between the 2D material and gold substrate. The results also suggest the coexistence of the 2D crystalline and amorphous polymorphs. STM measurements following sequential deposition of SiO and Fe followed by high temperature annealing in low pressure oxygen reveal ordered Fe silicate phases. Density functional theory and ab initio theory has been employed to identify stable Fe-Si-O phases on Au(111) and assess their potential for ferromagnetic coupling. A broader theoretical survey of magnetic coupling in first row transition metal layered silicates has identified structural motifs that favor ferromagnetic order.

2D-Contributed On Demand-73 Transition Metal -Silicates at the 2-D Limit*,* ***Nassar Doudin****, K. Saritas, S. Ismail-Beigi, E. Altman,* Yale University

Low-dimensional materials display novel emergent properties at the forefront of solid-state physics and chemistry and thus are of both fundamental scientific and applied technological interest. Here, van der Waals (VDW) materials at the 2-D limit, that is transition metal silicates in "quasi-bilayer" phases, supported on a different metal surface (e.g., epitaxial metal film[1]). The electronic and elastic coupling of the oxide nanophase to the underlying metal support creates a hybrid system with novel physical and chemical properties that are not shared by the individual constituents. I will investigate two topics in this talk: i) a 2-D oxide phase, which we have prepared by a solid state chemical reaction in two dimensions; and ii) a post-growth hydroxylation study of Fe-silicates on Pd(111) and Au(111) surfaces by using H_2O, H_2, and O_2 as probe molecules, both to gauge the electronic and chemical properties of the M-silicates systems and to investigate its functioning as multiferroic materials in the future. In the first part of the talk, I will concentrate on new structure concepts and their relation to the electronic and magnetic behavior of 2-D systems. In the case of the Fe-silicates, I will introduce a new approach to fabricate well-ordered oxide systems in low dimensions. The computational studies further reveal that the M-silicates (M= Fe, Co, Ni, Mn)can be stable, and further that the transition metal oxidation state may be tuned through the M:Si ratio and by altering the hydroxylation of the layer.[2]

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2D-Contributed On Demand-76 Designing Transition Metal Dichalcogenide Alloys for Photonic Integrated Circuit Applications*,* ***Yifei Li****, R. Jaramillo,* Massachusetts Institute of Technology

Transition metal dichalcogenides (TMDs) exist in several polymorphs including 2H (usually semiconducting), and 1T/1T' (usually semi-metallic). Our theoretical calculations and experimental measurements show that TMDs are optically-dense and can feature a difference in refractive index greater than unity between phases in the near-infrared (NIR). Fast, non-thermal martensitic phase-change behavior has been observed in TMDs, and transformation strains are expected to be low due to the layered crystal structure. For these reasons, we suggest that TMDs may be useful as active materials to control the phase of light in integrated photonic circuits, surpassing the performance of traditional phase-change materials.

Sulfide TMDs are attractive for application to photonics because they present lower optical loss and higher material stability than selenides or tellurides. However, sulfide TMDs also have higher transformation energy barriers. We address this problem by designing sulfide TMD alloys that are thermodynamically-adjacent to phase boundaries. We use density-functional theory (DFT) and the quasi-harmonic approximation to calculate free energy-composition diagrams at finite temperature for polymorphs in the MoS_2-TiS_2-ZrS_2 system. Our calculations predict that the free energy difference between phases can be reduced to near-zero through alloy design. We then synthesize sulfide TMD thin films through a two-step process of metal sputtering, followed by sulfurization in H_2S in a chemical vapor deposition (CVD) furnace. This two-step method, combined with combinatorial sputtering, enables rapid exploration of composition space and phase boundaries. By controlling the CVD furnace conditions, and in particular the trace oxygen concentration, we are able to lower the processing temperature for large-area alloy thin films below 500 °C; this is important for yielding good film morphology and for photonic integrated circuit integration. Finally, we demonstrate a test concept to study phase-change behavior with electrical stimulation and optical readout for a composition spread across a wafer, and we characterize the phase-change behavior of sulfide TMD alloys by Raman spectroscopy, spectroscopic ellipsometry, and infrared spectroscopy.

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2D-Contributed On Demand-79 Direct Imaging of Optoelectronic Properties at Atomically-Thin Semiconductor-Metal Buried Interface*,* ***Kiyoung Jo****, P. Kumar, S. Anantharaman, D. Jariwala,* University of Pennsylvania

Metal contact to two-dimensional semiconductor-Metal is one of the most consequential for high performance and highly scaled electronic and optoelectric devices. For example, fermi-level pinning in semiconductor-metal interface causes non-idealities in any device operation resulting in parasitic energy dissipation when electrical carriers diffuse from metal to semiconductor. Yet, the chemistry of the contact is poorly understood because semiconductor-metal contact is buried interfaces which make it difficult to probe directly. However, for 2-dimensional transition metal dichalcogenides, signals from semiconductor-metal interface are not screened out due to its atomically thin nature. In this talk, we will present spatial imaging of optoelectronic characteristics at the interface. Using a unique metal-assisted flipping technique, it is possible to access the optical and electronic properties of the buried interface. Taking advantage of scanning tip microscopy coupled with spectroscopy, we conducted kelvin probe force microscopy (KPFM), conductive-AFM, tip-enhanced Raman and photoluminescence spectrum, leading to concurrent map of electrical potential, conductivity, charge density, strain and emission spectra at the interface with deep-subwavelength (~20 nm) spatial resolution. We observe that direct evaporation of Au on monolayer MoS_2 creates ohmic contact reaching resistivity of 138 kΩ µm due to large strain of ~5% in the monolayer MoS_2 surface and charge transfer. MoS_2/*h*-BN/Au structure fabricated by the same technique reveals that intimate contact between monolayer MoS_2 and Au is critical for the strain and charge transfer effect. Different contacts out of different types of metal (Au, Ag, In/Au alloy) are explored, revealing that In/Au alloy-MoS_2 records lowest contact resistivity of 63 kΩ µm. The differences in contact quality is attributed to different levels of intimacy between MoS_2 and metal as well as defect creation during metal growth and cooling. Our result emphasizes that the importance of metal deposition schemes and paves a way towards engineering low resistance contacts.

2D-Contributed On Demand-82 Two-Dimensional High-Entropy Transition Metal Dichalcogenide Alloys*,* ***Aditya Deshpande****,* University of California Los Angeles*; C. Ratsch,* Institute for Pure and Applied Mathematics, UCLA*; C. Ciobanu,* Colorado School of Mines, USA*; S. Kodambaka,* University of California Los Angeles

Layered van der Waals (vdW) transition metal dichalcogenides (TMDCs) with the chemical formula MX_2 (M = transition metal from Groups 4-7 and X = S, Se, Te) are a family of widely studied materials that have expanded the range of electronic and electrochemical properties associated with two-dimensional (2D) materials, and their potential technological applications. In this work, we use density functional theory calculations for monolayer TMDCs with multiple cation species to point out the exciting possibility to further expand the range of 2D materials (and their properties) by showing that TMDCs with as many as five cation species, dubbed high-entropy TMDC (HETMDC) can be stable in either the 2H or 1T phases at temperatures between 100 K and 500 K. We have used random alloys of five cations (out of a total of nine cations) and showed that over 200 high-entropy TMDC alloy monolayers are likely to be realized experimentally in 2H or 1T phases, and also have shown that the stacking of such monolayers remains governed by vdW interactions. We have evaluated the sulfur vacancy formation energies in multication alloys and estimated the vacancy populations for a wide range of temperatures. We have found that HETMDC alloys display significantly larger vacancy populations compared to simple TMDCs at the same temperatures, due to a very wide range of vacancy formation: these results imply that the catalytic activity of HETMDC is vastly superior to TMDCs, hence illustrate the possibility of high-activity catalysts based on HETMDCs.

2D-Contributed On Demand-85 Doping of $MoTe_2$ via Surface Charge Transfer in Air*, Cristian Ciobanu,* Colorado School of Mines*; G. Stan,* NIST*; S. Likith,* Colorado School of Mines*; A. Rani, S. Zhang, C. Hacker, S. Krylyuk, A. Davydov,* NIST

Doping is a key process that facilitates the use of semiconductors for electronic and optoelectronic devices, by which the concentration and type of majority carriers (electrons or holes) can be modified controllably to achieve desired conduction properties. We report that changes in the surface potential of MoTe2 are determined by air adsorbates and the number of layers of exfoliated material. Changes measured in surface potential and work function could be attributed to the permanent dipole of the adsorbed molecule as well as to the charge transfer between the surface and the adsorbates (induced dipoles). Through density functional theory calculations we are able to remove this ambiguity, showing that (non-polar) oxygen molecules physisorb and drain electrons from the surface, thereby making it p-type and increasing its work function. This is in agreement with our Kelvin probe microscopy measurements; other adsorbates, such as water or hydroxyl, do not lead to agreement with the experimentally measured variations of the work function. Surface charge transfer doping (SCTD) driven by adsorbates can be easily adjusted through thermal annealing of the entire sample, leading to an effective modulation of the surface potential of MoTe2. Furthermore, we also illustrate local control of the surface charge doping by contact electrification using the probe of an electrostatic force microscope as a floating gate. After annealing or contact electrification, the air-exposed MoTe2 surfaces exhibit a slow reversal processes of re-adsorption of oxygen, restoring of the p-type doping. These investigations can complement typical field effect transistor measurements used to extract electronic transport properties of devices based on 2D materials. As a reversible and controllable nanoscale physisroption process, SCTD can thus open new avenues for the emerging field of 2D-TMDC electronics.

2D-Contributed On Demand-88 Stacking-Dependent Optical Properties in Bilayer WSe_2*, Kathleen McCreary,* *M. Phillips,* Naval Research Laboratory*; H. Chuang,* NOVA Research*; D. Wickramaratne,* Naval Research Laboratory*; M. Rosenberger,* University of Notre Dame*; C. Hellberg, B. Jonker,* Naval Research Laboratory

It has recently been demonstrated that the angle between layers of two-dimensional materials can strongly impact the resulting properties, inspiring the rapidly developing research area of twistronics. Here, we investigate stacking-dependent optical properties in bilayer WSe_2. Both 2H and 3R stacking orientations are synthesized by chemical vapor deposition. Samples are investigated using photoluminescence, Raman spectroscopy, and reflectivity measurements under ambient and cryogenic conditions. In both 2H and 3R systems, the A_{1g} Raman mode is sensitive to excitation conditions, with orders of magnitude enhancement observed for certain excitation wavelengths. However, the laser wavelength leading to maximum enhancement is distinctly different for the two stacking orientations, with 2H-WSe_2 exhibiting maximum enhancement under 514 nm excitation and 3R-WSe_2 at 520 nm excitation at cryogenic temperatures. DFT calculations and reflectivity measurements indicate differences in band structure between the two systems, evident by shifts in emission energy of excitonic features, and elucidate the source of variation in Raman spectra. Maximum Raman enhancement is achieved when the excitation wavelength is resonant with the stacking-dependent C-excitonic feature. This work provides a comprehensive investigation of optical properties in 2H- and 3R-WSe_2 bilayers.

2D-Contributed On Demand-91 Small Energy Gap Revealed in $CrBr_3$ Using Scanning Tunneling Microscopy and Spectroscopy (STM/S)*, Dinesh Baral,* *Z. Fu, A. Zadorozhnyi, R. Dulal, A. Wang, N. Shrestha, U. Erugu, J. Tang, Y. Dahnovsky, J. Tian, T. Chien,* University of Wyoming

Exploration of electronic and magnetic properties of 2D materials family is in a good advancement, with the goal of minimizing electronic devices towards atomic level. This family includes a huge range of materials- from insulators, semiconductors, metals to superconductors. In 2017, two independent groups demonstrated stable magnetic ordering in 2D vdW materials (CrI_3 and $Cr_2Ge_2Te_6$) [1,2] bringing in the ferromagnetic materials in 2D family. Since then, 2D magnetism has been discovered in various vdW materials, for example CrX_3 (X= Cl, Br, I) [3,4] among which $CrBr_3$ is the most air stable in CrX_3 family. Magnetic and optical properties of bulk $CrBr_3$ have been studied from 1960s. Despite the great attention in magnetic and optical properties, the electronic properties of $CrBr_3$ are relatively unexplored. Based on the various optical measurements, it is believed that $CrBr_3$ have an energy gap in the range of 1.68 – 2.1 eV[5,6]. Density fluctuation theory (DFT) reports show even higher deviations in the energy gap. These controversial results have indicated that the electronic properties of $CrBr_3$ is not well explored.

In this talk, I will present the result from STM/S of both thin and thick $CrBr_3$ flakes along with density fluctuation theory (DFT) calculations to reveal small energy gap to be 0.57 eV ± 0.04 eV[7]. This uncovering of small energy gap will solve the controversy and is the key to better understand the electronic properties of $CrBr_3$.

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2D-Contributed On Demand-94 Electrical Transport Properties of N- and P- Doped Inse: Bulk Crystals Versus Exfoliated Layers*, Zheng Sun,* The George Washington University*; S. Krylyuk,* National Institue of Standards and Technology*; P. Vora,* George Mason University*; M. Zaghloul,* The George Washington University*; A. Davydov,* National Institue of Standards and Technology

Efficient doping of van-der-Waals layered semiconductors, including carrier type, concentration and mobility, is challenging but essential for enabling their future electronic and photonic applications. Indium monoselenide, InSe, is a prime example of such layered materials with promising optoelectronic properties, which can be exfoliated down to few-nanometer-thin layers for device applications. This poster reports on substitutional n- and p- doping of InSe by introducing Sn and Zn dopants, respectively, in the Bridgman bulk crystal growth. Electrical transport properties of undoped vs. n- and p- doped InSe crystals are compared by conducting Hall measurements on the bulk InSe crystals and FET transport measurements on exfoliated thin layers. Undoped InSe is intrinsically n-type in both bulk and thin-film forms, with [n]~$3.5 \cdot 10^{14}$ cm^{-3} and m values of up to 1,400 $cm^2 \cdot V^{-1} \cdot s^{-1}$ for thick layers at 300K. Carrier concentration in Sn-doped thick layers increases approximately two-fold, while the corresponding mobility reduces ~2 times at 300 K. Zn-doped InSe shows p-behavior for bulk InSe with [p]~$7.9 \cdot 10^{13}$ cm^{-3} and m ~ 43 $cm^2 \cdot V^{-1} \cdot s^{-1}$ at 300 K, which reverts to ambipolar or n-type behavior for thin layers in FET devices.

2D-Contributed On Demand-97 Electronic Characterization Using Scanning Tunneling Microscopy and Spectroscopy of Solution-Synthesized Graphene Nanoribbons With Functional Groups*, Abigail Berg,* University of Illinois at Urbana-Champaign*; G. Li, A. Sinitskii,* University of Nebraska - Lincoln*; J. Lyding,* University of Illinois at Urbana-Champaign

We present the electronic characterization of a bottom-up solution-synthesized heterostructure made of the 9-A and chevron graphene nanoribbon (GNR) with $C_{10}H_{21}$ functionalized side chains. Atomically precise graphene nanoribbons with functional side chains have the potential of being connected to DNA origami scaffolding as a method of achieving deterministic GNR length and precursor arrangement. We use the dry-contact transfer (DCT) method to exfoliate the GNRs onto clean Si(100) in a room temperature ultra-high vacuum (UHV) scanning tunneling microscope (STM). The bandgap and density of states are probed using scanning tunneling spectroscopy (STS). We find that there is a semi-transparency effect across the bulk of the GNR most likely due to random C-Si bonds forming at the GNR-substrate interface. There is also an induced doping effect on the substrate next to the GNR which is most pronounced along the top and bottom edges of the GNR.

2D-Contributed On Demand-100 Observation of Electrically Tunable van Hove Singularities in Twisted Bilayer Graphene from NanoARPES*, Ryan Muzzio,* Carnegie Mellon University*; A. Jones, P. Majchrzak, S. Pakdel,* Aarhus University, Denmark*; D. Curcio,* aarhus University, Denmark*; K. Volckaert, D. Biswas,* Aarhus University, Denmark*; J. Gobbo, S. Singh,* Carnegie Mellon University*; J. Robinson,* Naval Research Laboratory*; K. Watanabe, T. Taniguchi,* National Institute for Materials Science, Japan*; T. Kim, C. Cacho,* Diamond Light Source, UK*; N. Lanata, J. Miwa, P. Hofmann, S. Ulstrup,* aarhus University, Denmark*; J. Katoch,* carnegie Mellon University

The possibility of triggering correlated phenomena by placing a singularity of the density of states near the Fermi energy remains an intriguing avenue toward engineering the properties of quantum materials. Twisted bilayer graphene is a key material in this regard because the superlattice produced by the rotated graphene layers introduces a van Hove singularity and flat bands near the Fermi energy that cause the emergence of numerous correlated phases, including superconductivity. Direct demonstration of electrostatic control of the superlattice bands over a wide energy range has, so far, been critically missing. This work examines the effect of electrical doping on the electronic band structure of twisted bilayer graphene using a back-gated device architecture for angle-resolved photoemission measurements with a nano-focused light spot. A twist angle of 12.2° is selected such that the superlattice Brillouin zone is sufficiently large to enable identification of van Hove singularities and flat band segments in momentum space. The doping dependence of these features is extracted over an energy range of 0.4 eV, expanding the combinations of twist angle and doping where they can be placed at the Fermi energy and thereby induce new correlated electronic phases.

2D-Contributed On Demand-103 2020 AVS Graduate Research Awardee: Scanning Tunneling Microscopy Studies of Carbon-Based Nanostructures Grown Through Competing on-Surface Interactions and Chemistry*, Jeremy Schultz,* *N. Jiang,* University of Illinois at Chicago

Intermolecular and molecule-substrate interactions are paramount to on-surface chemistry, where highly localized chemical environments determine physical properties and dynamic processes. Scanning tunneling microscopy (STM) enables the ability to probe individual atoms and molecules, revealing local electronic effects and structure. STM was used to study a common method used to develop two-dimensional nanocarbon structures. The Ullmann-like coupling reaction is induced by a metal substrate, involving the the dissociation of an aromatic carbon-halogen bond which allows for covalent intermolecular coupling. We extend this reaction method to consider the effects of the inclusion of a catalytically active diketonic group within the structure of the precursor molecule. Additionally, the process was found to critically depend on the substrate identity.

On Ag(100), the precursor 3,6-dibromo-phenanthrequinone (DBPQ) molecules were found to self-assemble through hydrogen and halogen interactions, resulting in well-ordered molecular islands which impacted the organometallic structure ultimately formed after reaction. The metal-organic coordination networks that formed following thermal annealing were found to arise from the competition between C⋯Ag⋯C and C=O⋯Ag interactions [1]. On Au(100), two competing intermediate dimers were possible, cis and trans forms. The cis form was preferentially present on the bare Au(100), and the trans form occurred within atomic bromine networks that formed on the surface with total selectivity. The cis dimers were found to terminate at tetramers, as steric hindrance prevented the formation of longer oligomers. While the trans dimers could result in longer polymeric chains. Utilization of increasing coverage resulted in the selective formation of long polymer chains proceeding through the bromine stabilized trans dimers [2]. This work highlights the consequences of the inclusion of functional groups in the precursor molecule, as well as the roles of initial self-assembly, competing fundamental interactions, and leaving groups in steering reaction-based bottom-up assembly.

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2D-Contributed On Demand-106 Band Structure and Electronic Properties of Edge-Functionalized Germanene Nanoribbons*, Alexander Goldstone,* *Q. Li,* George Mason University

In the wake of the discovery of graphene, the search for new and remarkable 2D materials with astounding electronic and mechanical properties has led to the fabrication of germanene, a 2D germanium allotrope similar to silicene. Unlike the planar structure of the graphene lattice, germanene has a buckled honeycomb structure with two vertically displaced sublattices. Free-standing germanene is a semimetal, where the electrons behave as massless relativistic particles leading to enhanced carrier mobility. Indeed, recent studies have shown germanene to have an intrinsic carrier mobility on the order of 6x10^5 cm^{2}V^{-1}s^{-1}[1], an order of magnitude greater than graphene's. Another advantage over graphene is germanene's larger spin-orbit gap (23 meV)[2], which when compared to graphene's (<0.05 meV) makes germanene a superior candidate to exhibit the quantum spin Hall effect at experimentally viable temperatures. Lastly, the germanene lattice allows for an opening of the band gap via an applied electric field or adsorption of foreign atoms, enabling the creation of germanene based field-effect devices. In this study we analyze the effect of edge passivating species H, C, N, P, As, O, S, Se, Te, F, Cl, Br, and I on the electronic and spin-orbit properties of germanene armchair and zigzag nanoribbons. For each species, the effect of width and strain on the band structure is examined, as well as the magnetic moment and spin orbit gap of the nanoribbons to explore potential applications for spintronic devices. We found that for each passivating species, the armchair nanoribbons transition between semiconductor and semimetal in a cyclical pattern depending on width. The bandgap of the nanoribbon, as well as the semimetal point, are tunable through width, passivation species, and mechanical strain. In the case of zigzag germanene nanoribbons, the material remains a semimetal regardless of width, but the nature of the band structure varies significantly among different passivation species with some displaying potential superconducting properties. The different passivation species reveal distinct groups showing similarities in both the geometric structure and band structure of the nanoribbons over various widths. Using machine learning we attempt to classify these passivation species into distinct groups that generate nanoribbons with similar physical and electronic properties.

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2D-Contributed On Demand-109 Non-Enzymatic Electrochemical Sensing of H_2O_2 Based on 2d Tellurene*, Netanya Dennis,* *F. Yan, M. Garcia Cervantes, B. Chitara,* North Carolina Central University

2D tellurene (Te) nanosheets have recently emerged as promising building blocks for nanoscale high-performance electronic and optoelectronic devices due to their unique electrical and optical properties. Here, we report the synthesis of large-area, high-quality 2D Te nanosheets using a facile one-pot hydrothermal approach, and demonstrate for the first time their use for electrochemical detection of hydrogen peroxide (H_2O_2) with micromolar sensitivity. The as-synthesized 2D Te nanosheets were characterized by Raman spectroscopy, scanning electron microscopy, and atomic force microscopy. The electrochemical performance of 2D Te nanosheets was examined by cyclic voltammetry and amperometry. The 2D Te nanosheets-based sensor shows selective detection of H_2O_2 in the presence of higher concentrations of common interfering substances in human sweat, including NaCl, ascorbic acid, uric acid, and dopamine. An exploration of the feasibility of this methodology for glucose detection in artificial human sweat is currently underway. The findings reported here shed new light on the development of a new generation of flexible and wearable glucose sensors based on 2D materials.

2D Materials
Room On Demand - Session 2D-Invited On Demand
2D Materials Invited On Demand Session

2D-Invited On Demand-7 Tuning Energy Levels and Energy Flow in Nanomaterials Using the External Environment*, Archana Raja,* Lawrence Berkeley National Laboratory **INVITED**

The interaction between charge carriers in atomically thin, quasi-two-dimensional (2D) materials is strongly influenced by the local environment. I will discuss how tuning the external dielectric screening can modify the band gap and exciton energies in 2D transition metal dichalcogenides, allowing the formation of lateral heterojunctions without modifying the material itself [1]. Furthermore, using a combination of optical and angle resolved photoemission spectroscopies with microscopic spatial resolution, we show that the band structure rigidly shifts in response to the change in local dielectric screening [2]. This environmental sensitivity can also lead to a new type of disorder that leads to spatially inhomogeneous band gap and exciton energies as a consequence of spatial variations in the external dielectric screening rather than any material imperfections [3]. I will also briefly discuss new experimental approaches to the study of interfacial phenomena in 2D heterostructures and the associated ultrafast dynamics. In addition to the intrinsic scientific interest in understanding materials in this distinctive regime, such control offers a non-invasive approach to engineer material properties by tuning the local environment rather than the material itself, yielding a new paradigm for nanoscale devices.

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2D-Invited On Demand-13 Atomic-Scale Study and Engineering of Low-Dimensional Materials*, Jani Kotakoski,* University of Vienna, Austria **INVITED**

Despite the great promise of two-dimensional materials due to their exciting properties, they are not always directly suitable for applications. One way to tune the material properties is to manipulate the atomic structure using particle irradiation. However, as one might expect, this is challenging to do in the case of extremely thin materials, where careful control over the irradiation energy and solid understanding of the underlying atomic-scale phenomena are required. Despite the challenges, electron and ion irradiation have recently evolved into powerful techniques to manipulation the atomic structure of two-dimensional materials. At the same time, the recent advancements in aberration-corrected transmission electron microscopy both provide means to directly image the manipulated structures but also to fine tune them by inducing local structural changes and even to move defects and impurity atoms.In this presentation, I will show that low-dimensional materials change shape due to van der Waals interaction within heterostructures, describe the advances in manipulating low-dimensional materials with electron irradiation, including nanometer-range chemical etching and directed diffusion of impurity atoms, and provide an overview of our latest results in using ion irradiation at a large energy scale to modify 2D materials via introduction of foreign atoms and nanopores. Finally, I will also demonstrate that transmission electron microscopy can be incorporated as an integral part of a ultra-high vacuum setup with different possibilities for experimentation before, during and after atomic-resolution microscopy, including the growth of novel 2D materials using free-standing graphene as the substrate.

2D-Invited On Demand-19 Electronic Structures of Two-Dimensional Topological Materials*, Sung-Kwan Mo,* Lawrence Berkeley National Laboratory **INVITED**

Due to the quantum confinement and changes in the symmetry, electrical and topological properties of atomically-thin two-dimensional (2D) materials are often largely different from those of their bulk counterparts. In this talk, I will focus on the changes in topological properties in 2D layers, which is explored by combining bottom-up growth using molecular beam epitaxy (MBE), in situ angle-resolved photoemission (ARPES), scanning tunneling microscopy/spectroscopy (STM/STS), and first principle calculations. We have found that the topological properties of 2D materials can be tuned by thickness, lateral interface, strain, and electric field. The material systems under discussion include 1T'-WTe_2 [1], 1T'-WSe_2 [2], alpha-Sn [3] and Na_3Bi [4].

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2D-Invited On Demand-25 2020 AVS Medard W. Welch Award Lecture: Chemically Tailoring Interfaces in Two-Dimensional Heterostructures*, Mark Hersam*[1]*,* Northwestern University **INVITED**

As a result of their unique electronic, optical, and physical properties, two-dimensional (2D) materials are actively being explored for applications in next-generation computing [1], quantum information science [2], and energy technologies [3]. With exceptionally high surface-to-volume ratios, 2D materials are highly sensitive to their environment, resulting in a strong dependence of their properties on substrate effects, extrinsic adsorbates, and interfacial defects. Furthermore, the integration of 2D materials into heterostructure devices introduces further demands for controlling interfaces with atomic precision. With this motivation, this talk will explore emerging efforts to understand and utilize interfacial chemical functionalization to influence the properties of 2D heterostructures. For example, organic adlayers can tailor chemical reactivity to enable conformal atomic layer deposition of pinhole-free encapsulation layers that mitigate the deleterious effects of ambient exposure, particularly for ambient-unstable 2D materials such as black phosphorus and monochalcogenides [4]. The integration of organic self-assembled monolayers with 2D semiconductors also allows for tailoring of electronic and optical properties such as photoinduced charge separation in fullerene/InSe heterojunctions [5] and mixed-dimensional excitonic states in phthalocyanine/MoS_2 heterojunctions [6]. By exploiting spatially inhomogeneous surface chemistry, seamless lateral 2D heterostructures can also be realized including perylene/borophene [7] and graphene/borophene [8] heterostructures, each of which show atomically sharp electronic interfaces as confirmed by ultrahigh vacuum scanning tunneling microscopy and spectroscopy. Overall, by providing substantial tailoring of interfaces, chemical functionalization presents opportunities for improved functionality in 2D heterostructure devices.

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2D-Invited On Demand-31 First-Principles Calculations of 2D Materials for Gas Sensing Applications*, Udo Schwingenschlogl,* KAUST, Saudi Arabia **INVITED**

We study the potential of material simulations based on first-principles methods to predict gas sensing properties of 2D materials. This emerging class of materials is of particular interest to gas sensing applications due to high surface-to-volume ratios and chemical stability. We discuss in detail results of electron transport calculations within the Landauer-Büttiker formalism and compare the conclusions to analyses in terms of adsorption energies, charge transfers, and work functions. Specific examples include the effects of the interlayer interaction in bilayer MoS_2 and WS_2 on the gas sensing performance and the consequence of the presence of reactive Si in Si_2BN. We also address the properties of C_3N and para/meta-C_3Si. Potential of very sensitive gas sensing is demonstrated for para-C_3Si and is explained by the susceptibility of Dirac states to symmetry breaking distortions rather than by a mechanism based on charge transfer. Finally, the enhanced gas sensing performance of monovacant C_6BN is studied and it is shown that the work function changes of both pristine and monovacant C_6BN during gas adsorption do not correlate with the changes observed in the I-V characteristics.

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[1] **AVS 2020 Medard W. Welch Awardee**

2D-Invited On Demand-37 Modeling the Growth of 2D Crystals: Analytical, Phase-Field and Machine Learning Methods*, **Vivek Shenoy,*** University of Pennsylvania **INVITED**

Vertical stacking of monolayers *via* van der Waals (vdW) interaction opens promising routes toward engineering physical properties of two-dimensional (2D) materials and designing atomically thin devices. Increasingly, the bottleneck in this field is the controlled synthesis of these materials through methods such as chemical etching and chemical vapor deposition (CVD). In this talk, I will present insights into synthesis and growth of 2D materials developed from analytical, phase-field, and machine learning models. First, we adapt the state-of-the-art positive and unlabeled (PU) machine learning framework to predict which theoretically proposed 2D materials in the MXene family have the highest likelihood of being successfully synthesized. By considering both the MXenes and their precursors, we identify 18 MXene compounds that are highly promising candidates for synthesis. Next, we develop a general multiscale model for scalable CVD growth of layered materials and predict the necessary growth conditions for vertical (initial + subsequent layers) *versus* in-plane lateral (monolayer) growth. An analytic thermodynamic criterion is established for multilayer growth that depends on the sizes of both layers, the vdW interaction energies, and the edge energy of 2D layers. We connect the model to experimental controls and find that temperature and adatom flux from vapor are the primary criteria affecting the self-assembled growth. This model agrees with experimental observations of various monolayer and bilayer transition metal dichalcogenides grown by CVD. Finally, we consider CVD synthesizable transition metal dichalcogenide heterostructures as a robust platform for engineering quantum confinement of Dirac fermions using a multiscale model for electronic properties.

Actinides and Rare Earths Focus Topic
Room On Demand - Session AC-Contributed On Demand
Actinides and Rare Earths Contributed On Demand Session

AC-Contributed On Demand-1 Characterization of Uranium Oxide Corrosion Using a Microfluidic Electrochemical Cell*, **Jennifer Yao**, E. Buck, S. Tripathi, N. Lahiri, E. Ilton, S. Riechers, D. Reilly,* Pacific Northwest National Laboratory*; S. Chatterjee,* TerraPower LLC*; X. Yu,* Pacific Northwest National Laboratory

Study of UO_2 corrosion is important in understanding the spent nuclear fuel (SNF) disposal. To address the challenges in investigating large amount of SNF materials, we developed a new approach to incorporate UO_2 powder onto the working electrode of a microfluidic electrochemical cell, aka the system for analysis at the vacuum liquid interface (SALVI) E-cell, to facilitate UO_2corrosion study at the microscale. Instead of using bulk spent fuel pieces as working electrode at the macroscale, UO_2 powder was mixed withpolyvinylidene fluoride (PVDF) and carbon black to form the working electrode with mm dimension and included into the SALVI E-cell. The UO_2 powder electrode went through electrochemical corrosion in 0.1 M $NaClO_4$ (pH=9.5) aqueous electrolyte using the electrochemical station. Multimodal imaging analysis, including in situ scanning electron microscope (SEM) coupled withEnergy-dispersive X-ray spectroscopy (EDS) as well as ex situ transmission electron microscopy (TEM) and atomic force microscopy (AFM), was applied to reveal the morphological change, oxidation layer distribution, and topographical information of UO_2 before and after corrosion.In addition, X-ray photoelectron spectroscopy (XPS) was used to determine the oxidation state of the UO_2 electrode surface disassembled from the microfluidic E-cell after anodic oxidation. Our results demonstrate a promising approach to characterizing UO_2 corrosion at the microscale using multimodal imaging. Particularly, in situ SEM imaging and EDS mapping allow direct observation of corrosion in liquid. This new approach is useful in studying the interaction between geological repository environments (e.g., groundwater) and SNF to validate and improve the Fuel Matrix Dissolution Model.

AC-Contributed On Demand-4 Observation of Multiple Dirac States in a Magnetic Topological Material $EuMg_2Bi_2$, ***Firoza Kabir,*** University of Central Fllorida*; M. Hosen,* University of Central Florida*; F. Cheenicode-Kabeer, A. Aperis,* Uppsala University, Sweden*; X. Ding,* Idaho National Laboratory*; G. Dhakal, K. Dimitri, C. Sims, S. Regmi, L. Persaud,* University of Central Florida*; K. Gofryk,* Idaho National Laboratory*; P. M. Oppeneer,* Uppsala University, Sweden*; D. Kaczorowski,* Polish Academy of Sciences, Poland*; M. Neupane,* University of Central Florida

Initiated by the discovery of topological insulators, topologically non-trivial materials, more specifically topological semimetals and metals have emerged as new frontiers in the field of quantum materials. In this work, we perform a systematic measurement of $EuMg_2Bi_2$, a compound with antiferromagnetic transition temperature at 6.7 K, observed via electrical resistivity, magnetization and specific heat capacity measurements. By utilizing angle-resolved photo emission spectroscopy in concurrence with first-principles calculations, we observe Dirac cones at the corner and the zone center of the Brillouin zone. From our experimental data, multiple Dirac states at Gamma and K points are observed, where the Dirac nodes are located at different energy positions from the Fermi level. Our experimental investigations of detailed electronic structure as well as transport measurements of $EuMg_2Bi_2$ suggest that it could potentially provide a platform to study the interplay between topology and magnetism.

AC-Contributed On Demand-10 Tuning Formation of Large Uranium Oxide Cluster Ions from the Surface of Depleted Uranium Under Static Bombardment Using Ga+ During ToF-SIMS*, **Shohini Sen-Britain**, A. Nelson,* Lawrence Livermore National Laboratory

Laser ablation (LA) mass spectrometric and static time-of-flight secondary ion mass spectrometry (ToF-SIMS) of metals produces similar ion distributions of large M_xO_y+ ions due to gas phase recombination reactions of small M_xO_y+ ions in the gaseous cloud formed during LA, or selvedge formed in static ToF-SIMS during ion sputtering [1].Specifically in the case of depleted uranium (DU), an expanded understanding of these recombination reactions due to ion sputtering under vacuum and in the presence of oxygen or in atmosphere can further our understanding of nuclear forensics and debris analysis [2, 3].We describe here precise control of large U_x+ and U_xO_y+ ion formation as a function of static ToF-SIMS Ga+ primary ion bombardment parameters.

We report the observation of large U_x+, U_xO_y+, and $U_xO_yH_z$+ ions (x = 1-14) during 25 keV Ga+ analysis of the DU surface oxide and sputter cleaned metal surface during primary ion bombardment under static conditions.These ions are large enough to suggest that intact cleavage from the DU surface is energetically prohibitive.Rather, collision cascade theory suggests that these large species are the product of post-ionization reactions in the selvedge of DU [4].Here, we report variation in the power law fits of secondary ion counts of U_x+, U_xO_y+ and $U_xO_yH_z$+ ions as a function of x (x=1-7) due to sputtering 2 nm into the DU surface oxide at ion current densities varying from 20 pA to 20 nA.We also report the variation of power law fits to secondary ion counts of U_x+ ions as a function of x (x = 1-14) due to tuning of instrument cycle time.Finally, we observe different rates of conversion of U_x+ ions to U_xO_y+ as a function of x during in-chamber surface oxidation under UHV conditions from residual moisture during static spectrum collection over a period of 3000 s.

Future applications of this work include monitoring of ion formation and variation in recombination reactions in the presence of oxygen, water vapor, and temperature.This work was also performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under contract DE-AC52-07NA27344.

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AC-Contributed On Demand-13 Hybridization Effect on the X-Ray Absorption Spectra for Actinide Materials*, W. Chiu,* University of California at Davis*; R. Tutchton,* Los Alamos National Laboratory*; G. Resta,* University of California at Davis*; T. Lin,* Rutgers University*; E. Bauer, F. Ronning,* Los Alamos National Laboratory*; R. Scalettar,* University of California at Davis*;* ***Jian-Xin Zhu,*** Los Alamos National Laboratory

Studying the local moment and 5*f*-electron occupations sheds insight into the electronic behavior in actinide materials. X-ray absorption spectroscopy (XAS) has been a powerful tool to reveal the valence electronic structure when assisted with theoretical calculations. In this work, we employed the DFT+Gutzwiller rotationally-invariant slave boson method to obtain the local Hamiltonian of the single-impurity Anderson model (SIAM), and used exact diagonalization (ED) method to calculate the XAS spectra from the model. An in-house built computational code was developed for the ED method. By applying this technique to the recently discovered 5*f*-electron topological Kondo insulator plutonium tetraboride (PuB_4), we were able to determine the signature of 5*f*-electronic correlation effects in the theoretical X-ray spectra. We found that the Pu 5*f*-6*d*hybridization effect provides an extra channel to mix the *j*=5/2 and 7/2 orbitals in the 5*f* valence. As a consequence, the resultant electron occupation number and spin-orbit coupling strength deviate from the intermediate coupling regime. We have also applied this approach to the δ-phase of Pu.

AC-Contributed On Demand-16 EXAFS as a Probe of Actinide Oxide Formation in the Tender X-Ray Regime*, James Tobin,* University of Wisconsin-Oshkosh*; S. Nowak,* SLAC National Accelerator Laboratory*; S. Yu,* Lawrence Livermore National Lab*; R. Alonso-Mori, T. Kroll, D. Nordlund, T. Weng, D. Sokaras,* SLAC National Accelerator Laboratory

Recent developments in Resonant Inelastic X-Ray Scattering Experiments have vastly improved the resolution in X-ray Spectroscopies such as X-ray Absorption.However, the use of Tender X-rays (~3keV) and the reactivity of actinides such as uranium have given rise to new questions about bulk and surface sensitivity, what constitutes a surface and how to characterize the formation of an oxide.It will be shown that the *in situ* electron scattering features that are part of the RIXS spectrum can be used to quantify the uranium oxide formation and determine cleanliness, independently of the near edge features that provide information about the unoccupied electronic density of states.

*J. G. Tobin,S. Nowak, S.-W. Yu, R. Alonso-Mori, T. Kroll, D. Nordlung, T.-C. Weng, D. Sokaras, "EXAFS as a Probe of Actinide Oxide Formation in the Tender X-Ray Regime," Surface Science **698**, 121607 (2020) https://doi.org/10.1016/j.susc.2020.121607.

AC-Contributed On Demand-19 Detection of Covalency in Pu(IV) Materials: Spectroscopic and Computational Tools*, Bianca Schacherl,* Karlsruhe Institute of Technology (KIT), Institute for Nuclear Waste Disposal (INE), Germany*; P. Bagus,* Center for Advanced Scientific Computing and Modeling (CASCaM) Department of Chemistry University of North Texas*; A. Beck,* Karlsruhe Institute of Technology (KIT), Institute for Nuclear Waste Disposal (INE), Germany*; M. Tagliavini,* Heidelberg University, Institute for theoretical physics, Germany*; M. Trumm,* Karlsruhe Institute of Technology (KIT), Institute for Nuclear Waste Disposal (INE), Germany*; M. Haverkort,* Heidelberg University, Institute for theoretical physics, Germany*; T. Vitova,* Karlsruhe Institute of Technology (KIT), Institute for Nuclear Waste Disposal (INE), Germany

Plutonium has a complex electronic structure, where the role of the 5f orbitals in chemical bonding and the level of covalency has not been understood in detail and is a very active field of research. Resonant inelastic X–ray scattering (RIXS) is a valuable tool and can lead to a deeper understanding of the electronic structure of plutonium materials.[1,2] Also high-energy resolution X-ray absorption near edge structure (HR-XANES) has proven powerful in plutonium speciation studies.[3,4]

Relativistic quantum chemical computations for the Pu^{4+} ion and the PuO_2 compound were performed. We will discuss four computational measures of covalency of the Pu 5f orbitals. The $PuM_{4,5}$-edge HR-XANES and Pu $M_{4,5}$-edge core-to-core 3d4f RIXS on PuO_2 and other Pu^{4+} compounds under various experimental conditions were conducted at the INE and ACT beamlines at the Karlsruhe research accelerator (KARA) at KIT in Karlsruhe Germany.[5,6]

We found that for PuO_2 the Pu 5f covalent mixing with O valence orbitals overall is relatively small. It is the largest in the 5f(7/2) a_{2u} orbital with the highest orbital energy. The analysis of the Pu $M_{4,5}$-edge HR-XANES in combination with the calculated results, showed that the spectra can not be described with a simple one electron transition between individual 3d and 5f orbitals applying the dipole selection rule. There is considerable amount of redistribution of 5f electrons involved in both the Pu M_4-edge and the Pu M_5-edge absorption processes, i.e. shake-up excitations (J = 5f(5/2) to 5f(7/2)) take place. From the comparison of the computational results with the HR-XANES spectrum, it was found that the second peak in the Pu M_4-edge and the shoulder feature in the Pu M_5-edge spectrum are probing the 5f(7/2) a_{2u} orbital and are therefore expected to be sensitive to bond variations. It will be discussed how the different interatomic interactions affect the Pu $M_{4,5}$–edge core-to-core 3d4f RIXS map of PuO_2. The here presented spectroscopic and theoretical tools will help to advance the understanding of the electronic structure of Pu materials.

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AC-Contributed On Demand-22 Interrogating the Surface Chemistry of Nanoscale Uranium Oxides*, Liane Moreau,* *H. Johnson,* Washington State University

A thorough exploration of uranium oxide surface chemistry is critical to understanding UO_2 corrosion in the nuclear fuel cycle and potential for catalytic reactivity. Nanoscale uranium oxides provide a template through which to study the surface chemistry of actinide materials. Synthesis of actinide nanoparticles, however, has not been empirically well-developed, making investigations into their size- and surface-dependent properties relatively unexplored. Synthesis of nanoparticle constructs in the range between 2 and 100 nm utilizing colloidal and template-based approaches will be discussed, along with their structural attributes on the atomic and nanometer length scales. Characterization of such particles, in a manner which resolves surface chemistry, becomes challenging using conventional characterization techniques. In particular, the high curvature of nanoparticle surfaces and complex solution interface chemistry makes surface techniques appropriate to thin film systems insufficient structural probes.

We overcome the presented challenge through focusing on the study of ultrasmall nanoparticles, which present particularly high surface area to volume ratios. The high percentage of surface atoms makes bulk characterization techniques such as X-ray absorption spectroscopy (XAFS) become surface-sensitive probes, enabling us to resolve surface structure in atomistic detail. New models will be presented that provide an indication of elemental speciation of surface atoms and sites for surface ligand binding, through combining geometric models with structural parameters extracted from XAFS. Results obtained through this work are broadly applicable towards resolving nanoparticle surface chemistry and provide foundational methodology towards exploring the nanoscale properties of actinide oxides.

AC-Contributed On Demand-25 Broadening of the XPS Spectra of U Oxides*, C. Nelin,* Consultant*; **Paul S. Bagus,*** University of North Texas

It is common to attempt to improve the energy resolution of XPS in order to obtain more information about the electronic structure of the system studied. However, it may not be possible to improve the resolution because unresolved final states features are present which lead to broad features. These unresolved features may arise from closely spaced multiplets for the angular momentum coupling of the core and valence open shell electrons. They may also arise from excitations to higher lying vibrational levels for the final ionic states which may be especially important when bond distances for the core-ionized states are very different from those for the initial state; see, for example, Ref. [1]. When the energy separation of the final states are less than or comparable to the lifetime of the core-hole, it will not be possible to resolve the states and there will only be a broadening, often quite significant, for the observed peak composed of these unresolved features. Thus, for example, the $U(5f_{7/2})$ peak of UO_2 has a FWHM of 1.4 eV although the instrumental resolution was 0.3 eV. [2] Similar large FWHM have been observed for U in different oxidation states. [3] In order to be able to relate the widths of these broadened features to the chemical and physical interactions in the system, it is necessary to understand the separate contributions of the multiplet splittings and the vibrational excitations. It has been shown that, for U(IV) 4f XPS in UO_2, the contributions of the multiplet splitting and the vibrational excitations are comparable, each contributing ~0.5 eV to the FWHM. [2] In the present work, the contributions of these mechanisms are examined for U(V) and U(VI) oxidation states. In addition, the broadening is examined for the XPS of different core levels where the relative importance of multiplet and vibrational broadening is different from that for the U(4f)

XPS. The theoretical predictions for these different parameters can be validated paving the way to extract chemical information from the measured FWHM. [4] The theoretical framework for these predictions is based on wavefunctions for embedded cluster models of the oxide.

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AC-Contributed On Demand-28 XPS, UPS Study of Pure and Alloyed U Hydrides*, Oleksandra Koloskova,* *E. Tereshina-Chitrova, M. Paukov,* Charles University, Prague, Czech Republic*; T. Gouder,* European Commission, JRC. Institute for Transuranium Elements, Germany*; J. Kolorenč,* Institute of Physics, Czech Academy of Sciences, Czechia*; L. Havela,* Charles University, Prague, Czech Republic

Besides the fundamental importance, uranium hydride has considerable relevance for nuclear energy and devices, which motivates continuous effort to understand its formation and properties [1], in particular its electronic structure.

Photoelectron Spectroscopy is a method which directly probes the electronic structure. However, surface oxidation is an issue, which we overcome using the strategy of thin film synthesis. Surprisingly, it became possible to stabilize the UH_2 phase (non-existent as a bulk) in a thin film form [2].

XPS was first used for analysis of the samples quality. One of the difficulties is that the H-1*s* line is a part of the U valence band, hence it cannot be used to quantify the H concentration. We followed an empirical approach based on gradual increase of H_2 partial pressure in the working gas (Ar) while monitoring variations of the U-4*f* core-level spectra until saturation is reached [3].

Details of electronic states in the vicinity of the Fermi level are explored by UPS, surpassing XPS both by intensity and energy resolution (about 70 meV). Comparison of UPS spectra of U and UH_3 revealed that the spectra are similar just at the Fermi level (if properly normalized), the maximum for UH_3 is slightly displaced from the Fermi level to ≈140 meV binding energy. The U metal has DOS increasing up to the Fermi level and the Fermi-Dirac cutoff forms the maximum at 90 meV. Another feature of UH_3 (UH_2 is very similar) is the broad shoulder at 0.5 eV (ascribed to 5*f* multiplet from GGA+U calculations). Details of the DOS shape resist to a quantitative description using DFT calculations [1]. However, spectral density obtained from DMFT calculations captures both the maximum just below E_F and the 0.5 eV shoulder. This stresses the importance of electron correlations for the description of U hydrides.

As the XPS spectra of UH_3 and UH_2 are so similar, it is hard to distinguish which species was deposited. Magnetization measurements turned particularly useful. While both species are ferromagnets, their T_C values are different (165 K for UH_3 and 120 K for UH_2) [2]. Using the $M(T)$ dependence, we can assess the phase composition (pure UH_2, UH_3 or mixed-phase) of the samples.

This work was supported by the Czech Science Foundation under the grants No. 18-02344S and 21-09766S and b y the Grant Agency of the Charles University under Project No. 814120.

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AC-Contributed On Demand-31 Development of the High-T CDW in *REPt₂Si₂*, *Volodymyr Buturlim,* *P. Dolezal,* Charles University, Czechia*; E. Duverger-Nedellec,* Sorbonne Université, France*; A. Andreev,* Institute of Physics of the Czech Academy of Sciences, Czechia*; M. Falkowski,* Institute of Molecular Physics, Poland*; K. Gofryk,* Idaho National Laboratory*; L. Havela,* Charles University, Czech Republic

RPt2Si2 compounds form in the tetragonal non-centrosymmetric CaBe2Ge2 structure type both for lanthanides and actinides. The unifying pattern seems to be the CDW state, coexisting either with magnetic order or conventional superconductivity for rare earths. We identified that the generally recognized low-temperature CDW state setting in the first order transition is probably generally preceded by another CDW state, entered at a critical temperature close to 300 K via the second order transition, leaving less dramatic fingerprints in physical properties [1,2]. Here we will present results obtained using single-crystal XRD and high-precision dilatometry on selected single crystals along a- and c-axis. As one of the two Pt-Si slabs is most likely responsible for the instability towards the CDW formation, we believe that at least phenomenologically similar behavior of UPt2Si2 [3] indicates localization of the U-5f states in the U analogue. Possible involvement of the 5f states in bonding would arguably change the cohesion characteristics and the analogy of U with rare earths would be lost.

This work was supported by the Czech Science Foundation under the grants No. 18-02344S and 21-09766S.

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AC-Contributed On Demand-34 Electronic Structure and Spectroscopy of UH3 from the LDA+DMFT Perspective*, B. Chatterjee, Jindrich Kolorenc,* Institute of Physics, Czech Academy of Sciences, Prague, Czechia

We employ material-specific dynamical mean-field theory (LDA+DMFT) to investigate the electronic structure of UH3. We use the computed electronic structure to model valence-band photoemission and x-ray absorption spectra. We investigate the sensitivity of our results to the Coulomb U parameter that enters the LDA+DMFT method, since there is a large spread of recommended values reported in the literature, ranging from 0.5 eV [1] to more than 5 eV [2].

To understand the origin of certain spectral features, we analyze how the many-body eigenstates of the DMFT auxiliary impurity model evolve when the hybridization between the uranium 5f states and the hydrogen 1s states is ramped up from zero (ionic 5f3 model) to the realistic value. This theoretical experiment enables us to illustrate how some of the photoemission features relate to the final-state multiplets of the 5f3 to 5f2 transition. The LDA+DMFT method thus provides a solid ground for the earlier empirical interpretation of the photoemission spectra in terms of the 5f atomic multiplets [3].

This work was supported by the Czech Science Foundation under the grant No. 21-09766S.

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Actinides and Rare Earths Focus Topic

Room On Demand - Session AC-Invited on Demand

Actinides and Rare Earths Invited On Demand Session

AC-Invited on Demand-7 Identifying Structural Features That Result in Activation and Coupling of Vibrational Modes in Actinyl Materials*, Tori Forbes,* University of Iowa **INVITED**

Vibrational spectroscopy is a valuable characterization tool for actinide chemistry and provides important information on bond strength, oxidation state, and coordination environment.This is particularly true for high valent actinides, where the actinyl cation ($D_{\infty h}$) possesses symmetric and asymmetric stretching modes that are typically Raman and Infrared active, respectively.Complexity is introduced by lowering the symmetry of the actinyl moiety, which can cause activation of modes within the spectral window of interest.In addition, coordination of the actinyl cation by equatorial ligands or intermolecular interactions in the solid state can result in concerted motions that lead to unexpected signals within these systems. In this presentation, I will focus on the spectral analysis of neptunyl (NpO_2^+/NpO_2^{2+}) and uranyl (UO_2^{2+}) solid-state compounds and explore activation and vibrational coupling effects of these materials.Surface effects for both solid crystalline phases and U(VI) adsorption onto electrospun polymer fibers will also be discussed.

AC-Invited on Demand-13 Sulfur Containing Ligands for Actinide Separations: How Do They Work?*, Jenifer Shafer,* Colorado School of Mines **INVITED**

Trivalent actinide lanthanide separations are amongst the most beguiling on the periodic table. A typical approach to accomplishing these separations is the use of soft donors which preferentially interact with the actinides over the lanthanides. Certain sulfur containing ligands are very effective at accomplishing these separations, but not all sulfur donating ligands are effective at this separation. Consequentially, a spread from very limited to record breaking separation efficacy can be observed despite very limited adjustment to the sulfur electronic structure in some instances. Recent studies presented here suggest the solvation environment surrounding metal-ligand complex is a very relevant design optimization point when developing actinide-lanthanide separations based upon sulfur-donating ligands. This presentation will discuss three vignettes that compare aqueous sulfur donors, aryl dithiophosphinic acids and Cyanex 301 and how their metal-ligand interactions occur. These ligand systems will allow for the development of a preliminary design framework of relevant separations features for actinide-lanthanide separations using sulfur ligands.

AC-Invited on Demand-19 Tracking Uranium Speciation by Synchrotron Spectromicrosopy*, Jesse Ward,* Pacific Northwest National Laboratory **INVITED**

Synchrotron techniques have several attractive features for application in a nuclear forensics context. Soft X-ray spectromicroscopy can yield chemically-sensitive and element-specific information about particles at a sub-micron scale. Hard X-ray fluorescence (XRF) imaging shows greater sensitivity to trace elements compared to electron microscopy techniques, at a similar spatial scale, and does not require extensive sample preparation. This talk will present the results of a ~2-year study using scanning transmission X-ray microscopy (STXM) to track the physical and chemical changes in uranyl fluoride particles stored under different relative humidity conditions. In addition, this talk will present the initial results of a more recent study comparing XRF and electron microprobe analysis data from uranium particles with varying trace element profiles. These projects demonstrate some of the unique capabilities synchrotron facilities can bring to the field of nuclear forensics.

AC-Invited on Demand-25 The PreCalc Project: Multiscale Framework for Predicting Morphology of Plutonium Oxide Particles*, Lindsay Roy,* Savannah River National Laboratory **INVITED**

Nearly all of the plutonium in the world has been manufactured synthetically through large-scale separation and purification facilities.The different processes create specific isotopic, chemical, and physical characteristics, or signatures, and those can be organized to determine whether an interdicted nuclear sample is or is not consistent with a given process.One of the most common processes is the conversion of plutonium nitrate to oxide through Pu(IV) oxalate precipitation process. Recently it has been shown that the morphological and physicochemical signatures produced from laboratory-scale experiments do not translate linearly to the production process because inhomogeneous temperature and pressure gradients dramatically complicate the macroscopic picture.It is our assertion that multi-scale, multi-physics models can provide a basis for the prediction of specific properties, but the approach must capture the atomistic features of nonequilibrium dynamic phenomena at finite temperatures while maintaining relevance at the process scale.

In that context, this presentation will be an overview of the modelling efforts at SRNL to integrate multiple time/length scales for a description of the precipitation and calcination dynamics of PuO_2 from a production facility, entitled the PreCalc Project.This presentation will discuss the framework development and modeling progress thus far in the project.

AC-Invited on Demand-31 Chemical and Microstructural Analysis of Nuclear Fuels at Nano-Length Scale Using Atom Probe Tomography*, Mukesh Bachhav,* Idaho National Laboratory **INVITED**

Understanding the microstructural and chemical changes in irradiated metallic and oxide fuel is integral to research and development of fuel cycle programs. Fissioning of uranium isotope in metallic and oxide nuclear fuel produces about a hundred primary fission fragments, many of which are unstable and thus generate still other isotopes through their chains of decay. Chemical analysis on fission product is crucial in understanding the behavior for their long-term use in reactor. For instance, fission products such as noble gases xenon and krypton are retained within bubbles and pores in the fuel material. However, certain fraction is released into the free volume of the fuel rod, which can be a potential life-limiting phenomenon in nuclear fuel rods. Such a build-up of rod internal gas pressure can severely affect the integrity of fuel cladding. Thus, swelling behavior and fragmentation of the fuel is associated with types of fission products formed during fission process.It is therefore essential to determine the chemical nature of fission products formed in U based fuels in order to predict its long-term behavior under extreme irradiation and temperature condition. More often, these microstructural changes associated with irradiation of fuels takes place at nano-length scale. There are very few analytical techniques in the field of materials characterization, which can quantify chemical composition and correlate to their spatial distribution at near atomic scale.

In recent past, Atom Probe Tomography (APT) has established itself to be an effective technique for elucidating 3D chemical composition in materials at nanoscale for a wide range of structural materials used for nuclear application. Thanks to advances in laser assisted APT, sample preparation methods in shielded glove box and programing tools, APT is now reliably used to correlate microstructure, microchemistry and property changes in nuclear materials. APT datasets provide 3D atom-by-atom reconstructions of nanoscale volumes with isotope identification and has emerged as a highly effective technique, complementing the information from more established microscopies. In this study, we present detailed analysis on correlation of fission products to burnup of nuclear fuel using APT technique on two U based fuels (Metallic: U-Mo and oxide- UO_2). For metallic fuel, systematic analysis is carried out on low enriched U-Mo alloy with burnup of 52 % and 69 % for fission product analysis.Similar method used to determine the burnup gradient in UO_2 fuel pin, which possess thermal gradient across radial direction influencing the formation and migration of fission products. These results provided insight into fundamental understanding of fission products in ceramic and metallic nuclear fuels.

AC-Invited on Demand-37 Surface Properties of Actinide Dioxides; Crystal Growth and Catalysis*, Enrique Batista,* *G. Wang, D. Gonzalez, P. Yang,* Los Alamos National Laboratory **INVITED**

Actinide compounds, especially actinide oxides, play a critical role in many stages of the nuclear fuel cycle. The behavior of these materials under different conditions dictate aspects from crystal growth to disposal of spent fuels, and much of those properties start at the surface. In that way, catalytic reactions that can lead to unstable storage conditions stem from surface interactions with environmental species. Similarly, the morphology of crystal growth conditions is dictated by the stabilization or destabilization of different surfaces by ligands present in the solution environment. We have recently been focusing on surface properties induced by the presence of surface defects and surface interactions with environmental and non-environmental molecules. In this talk we present results of these studies for a series of actinide dioxides (AnO_2). We show how, under predicted conditions, one can control the morphology of growth, starting from nanoparticles to solids. The effect of surface defects is also analyzed as they can significantly affect the outcome, not only in morphology but also on the catalytic properties of the different exposed surfaces.

Atomic Scale Processing Focus Topic
Room On Demand - Session AP-Contributed On Demand

Atomic Scale Processing Contributed On Demand Session

AP-Contributed On Demand-1 Cu_2O Spontaneous Etching By Acetylacetone and Cu Atomic Layer Etching Using Sequential O_2 or O_3 and Acetylacetone Exposures*, Aziz Abdulagatov,* *J. Partridge,* University of Colorado at Boulder*; V. Sharma, C. Dezelah,* ASM Microchemistry Ltd., Finland*; S. George,* University of Colorado at Boulder

Copper atomic layer etching (ALE) has been performed earlier using sequential exposures of O_2 or O_3 and hexafluoroacetylacetone (Hhfac) [1].To avoid halogens in the reactants, this study explored Cu ALE using O_2 or O_3 and acetylacetone (Hacac) (See Supplemental Figure 1).Cu_2O spontaneous etching and Cu ALE were measured using in situ spectroscopic ellipsometry (iSE).The oxidation of the copper films was also examined including the effect of the O_2 or O_3 exposures on the surface morphology, chemical state and crystallographic structure.Additional studies were performed on Cu_2O powders to identify volatile etch products and structural changes after Hacac exposures.

The copper oxide films were obtained by O_2 or O_3 oxidation of metallic copper films at 250ºC.Atomic force microscopy (AFM) measurements revealed that Cu oxidation produced rough surfaces.X-ray diffraction (XRD) and x-ray photoelectron spectroscopy (XPS) measurements showed that the oxidized films were crystalline cubic Cu_2O.The iSE measurements determined that the thickness of these Cu_2O films was reduced linearly by consecutive exposures of Hacac during spontaneous etching.Additional iSE analysis determined that Cu ALE using sequential exposures of O_2 and Hacac removed Cu at 4.1 Å/cycle at 250°C (See Supplemental Figure 2).This etch rate during Cu ALE was obtained using reactant pressures of 20 and 0.250 Torr, and dose times of 0.5 and 1 s, for O_2 and Hacac, respectively.

Quadrupole mass spectrometry (QMS) investigations were conducted using Hacac exposures on Cu_2O powders at 250ºC to identify the volatile etch products.H_2O was observed as a product at the beginning of the Hacac exposure.H_2O is consistent with the disproportionation reaction Cu_2O + 2Hacac ® $Cu(acac)_2$ + Cu + H_2O.To verify the production of Cu during this disproportionation reaction, XRD analysis was performed on the Cu_2O powders after the Hacac exposures.The XRD results confirmed that Cu_2O was partially converted to Cu by the Hacac exposures.QMS also searched for the $Cu(acac)_2$ reaction product from the disproportionation reaction.Although no $Cu(acac)_2$ was detected by QMS, $Fe(acac)_2$ was observed from the exchange of $Cu(acac)_2$ with Fe on the reactor walls.

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AP-Contributed On Demand-4 In-situ Analysis of Surface Reactions for Plasma-Assisted Thermal-Cyclic Atomic Layer Etching of Tantalum Nitride,

Kazunori Shinoda, Hitachi , Japan*; M. Hasegawa,* Nagoya University, Japan*; H. Hamamura,* Hitachi , Japan*; K. Maeda, K. Yokogawa, M. Izawa,* Hitachi High-Tech, Japan*; K. Ishikawa, M. Hori,* Nagoya University, Japan

Isotropic atomic layer etching (ALE) offers the potential of atomically precise material removal with high conformality and high selectivity for future three-dimensional devices including nano-sheet gate-all-around field effect transistors (FETs). The authors have developed isotropic ALE for various materials such as Si_3N_4 and TiN by using the surface reactions of ammonium salt-based modified layers in CHF_3/O_2 plasma [1, 2].Although this kind of plasma is suited for forming ammonium salt-based modified layers on Si_3N_4 and TiN films, erosion of carbon hard masks is a concern due to the use of oxygen. In this work, both conventional CHF_3/O_2 plasma and an oxygen-free fluorocarbon-based plasma have been compared by using in-situ X-ray photoelectron spectroscopy (XPS) to examine the surface reactions for plasma-assisted thermal-cyclic ALE of TaN.

Cycles involving CHF_3/O_2 plasma exposure and heating were repeated. The exposure to CHF_3/O_2 plasma produced a modified layer on TaN. In-situ XPS analysis revealed that the TaN surface was modified in the plasma by forming N-H bonds and Ta-O-F bonds. The layer thickness was self-limiting with respect to the plasma-exposure time. After heating, non-volatile tantalum oxides remained on the TaN surface due to oxidation of the surface.

Cycles involving oxygen-free fluorocarbon-based plasma exposure and heating were repeated for developing TaN ALE to suppress oxide residues.This plasma consisted of hydrogen and fluorine that could form an ammonium-salt-based modified layer in both Si_3N_4 and TiN ALE, and it did not consist of oxygen that could erode carbon hard masks. The modified layer was produced on TaN after exposure to the plasma at −20°C. In-situ XPS analysis revealed that the layer contained N-H bonds and Ta-F bonds.The modification of the TaN surface in the plasma was self-limiting with respect to the plasma-exposure time. After heating, both the N-H bonds and Ta-F bonds disappeared completely. This result suggests that the modified layer was removed by heating. Thus, an applicable process for using carbon hard masks has been successfully demonstrated, and its surface reactions for thermal-cyclic ALE of TaN have been analyzed.

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AP-Contributed On Demand-7 A first-principle Investigation of the ALD Selectivity Driving Forces for the Area Deposition of TiO_2,

Yukio Kaneda, Sony Semiconductor Solutions Corporation, Japan*; E. A. Marques,* Katholieke Universiteit Leuven, Belgium*; S. Armini, A. Delabie, M. van Setten, G. Pourtois,* IMEC, Belgium

Area selective deposition (ASD) is one of the advanced patterning technologies for further nano-scale devices. ASD enables the growth of a film on certain substrates (referred to as growth areas in what follows) and not on the other (labeled as non-growth). However, it is commonly observed that the process is poisoned by an uncontrolled deposition in an undesired area, typically protected by a surface inhibiting treatment, hence leading to a selectivity degradation. The latter is explained by the absorption of precursors in a non-growth area that acts as a seed for the nucleation of particles.[1] Though diffusion aspects are playing a key role in the process, a large part of the selectivity is also controlled by the reactivity (thermodynamic) driving forces between the precursors and the substrates. Next to the selection of the ALD precursor, it is also crucial to understand how much other molecules and by-products, such as the compounds generated by the desorption of surface inhibitors, or by the decomposition of the ALD precursors, impact on the selectivity.

Therefore, improving an ASD process requires gaining a fundamental understanding on the different mechanisms that drive the selectivity degradation. In this context, we studied the thermodynamic driving force of different key chemical reactions occurring during the ALD deposition of TiO2, including precursor adsorption on the surfaces of the growth and non-growth area, precursor decomposition and clustering, reactions with by-products and inhibitor desorption, and analyzed the mechanism of selectivity degradation by first-principle calculations with statistical thermodynamic considerations.

In this presentation, we will illustrate how the combination of atomistic simulations with thermodynamic considerations helps to understand the precursor dependency reported for the selective deposition of TiO_2 on SiO_2 and on silylated surfaces by Soethoudt *et al.*[2] We hence modeled silicon/silicon oxide surface models terminated by either hydroxyl groups (to mimic a growth area) or tri-methyl-silyl groups (ALD inhibitor), and $TiCl_4$ and H_2O as the precursor and the oxidizer, respectively. From this analysis, we reproduced the temperature dependence of the selectivity. We also attributed the mechanism of selectivity degradation to the desorption of the methyl-silyl groups which is driven by temperature and reaction by-products.

We then expanded the exercise to a set of 25 commercially available Ti precursors and ranked their performances in terms of selectivity.

[1]Fabio Grillo, *et al*., *Chemistry of Materials***2020***32* (22), 9560-9572

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AP-Contributed On Demand-10 Scaling of InGaZnO to sub-40nm Regime Using Advanced Etch Techniques,

Shreya Kundu*, F. Lazzarino,* IMEC, Belgium

Since early 2000s, InGaZnO (IGZO)–based semiconductor oxide has been studied and prototyped as advanced thin film transistors (TFTs) in transparent electronic devices like high-definition flat panel displays[1]. Owing to a range of attractive properties such as high carrier mobility (w.r.t amorphous silicon), low OFF state leakage, and optimal BEOL compatibility; IGZO-TFTs are now being presented as the next-generation candidate for the DRAM technology[2]. In addition, due to its possibility to offer high current density, it is also being considered as Schottky diode-based selectors for high density cross-point memory applications[3]. While these attributes make IGZO a compelling novel material to investigate, a key challenge to enable its successful integration is its patterning into features of desired dimensions, especially at high scaling densities. Generally, metallic alloys are etched using halogen plasmas. However, a layer of IGZO exposed to a halogen produces non-volatile halide residues thereby creating a chemical etch stop and an incomplete patterning process. It has been reported that hydrocarbons (i.e. CH_4) can be used to pattern large IGZO structures as the organometallic by-products formed from IGZO are volatile[4]. Nevertheless, there is a trade-off – hydrocarbons are mainly used as passivating agents during conventional etching. This passivating effect from hydrocarbons is magnified at tighter pitches creating a chemical etch stop yet again. In short, the scalability of IGZO features using hydrocarbon etch pose a significant challenge. In this work, we evaluate the dual role of CH_4 during the patterning of IGZO for a range of CD/pitch combinations. Advanced etching methods i.e. CH_4-based atomic layer etching and plasma pulsing are used to enable high-density IGZO patterning[5,6]. We are successfully able to demonstrate well-separated IGZO features of CDs ≤ 20 nm in pitches down to sub-40 nm regime. This newly tailored etch is observed to be robust across different feature sizes and spacings, clearly exhibiting its potential to become a universal etch approach for IGZO as well as for IGZO-like materials such as InSnO and InZnO. The patterning effort focused on ensuring smooth sidewalls with negligible redeposition; limited tapering; good selectivity to electrode contact-friendly hard masks; minimal damage to IGZO stoichiometry and crystallography; and most importantly, emphasized the repeatability and uniformity generated from this advanced etch scheme.

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AP-Contributed On Demand-13 A Theoretical Investigation Into the Oxidative Etching of Ruthenium*, Neung-Kyung Yu,* *B. Shong ,* Hongik University, Korea (Republic of)*; J. Lee , W. Kim ,* Hanyang University, Korea (Republic of)

A theoretical investigation into the oxidative etching of ruthenium

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2 Materials Science and Chemical Engineering, Hanyang University, Ansan, Korea

Ruthenium (Ru) is a transition metal with low resistivity especially on a nanometer scale, making it a promising candidate for future interconnect applications. Ru can be oxidized and dry etched through the formation of volatile RuO_4 under oxidizing conditions [1]. This distinctive property makes Ru easily compatible with atomic layer etching (ALE) process, if a self-limiting process condition for the etch rate can be found. Moreover, since atomic layer deposition (ALD) of Ru utilizes oxidative counter-reactants, Ru can be used in bottom-up selective patterning processes combining ALD and selective etching [2]. Meanwhile, the atomistic mechanism of the oxidative etching process of Ru is not yet thoroughly determined. In this work, the mechanism of surface oxidation and dry etching of Ru under ozone environment is investigated using density functional theory (DFT) calculations. The explored pathways include surface oxidation of Ru and formation of ruthenium oxide (RuO_2), from both of which desorption of RuO_4 is considered. Our results suggest that direct etching from oxidized Ru surface is preferable to the decomposition of RuO_2 surface, indicating that there might be a process window for quasi-ALE of Ru.

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AP-Contributed On Demand-16 Blocking Thermal Atomic Layer Etching With Removable Etch Stop Layers*, David Zywotko,* University of Colorado Boulder*; O. Zandi, J. Faguet, P. Abel,* TEL Technology Center, America, LLC*; S. George,* University of Colorado Boulder

Thermal atomic layer etching (ALE) can be performed using sequential fluorination and ligand-exchange reactions. For example, thermal Al_2O_3 ALE can be achieved using HF for fluorination and $Al(CH_3)_3$ (trimethylaluminum (TMA)) as the metal precursor for ligand-exchange [1]. Sequential exposures of HF and TMA lead to Al_2O_3 etch rates of 0.47 Å/cycle at 285°C. The ability to block thermal ALE selectively will be useful for advanced nanofabrication. This study demonstrates how thermal Al_2O_3 ALE can be blocked with removable ZrF_4 etch stop layers. In situ quartz crystal microbalance (QCM) measurements were utilized to monitor the etching and the effect of the etch stop layers.

The ZrF_4 etch stop layers could be deposited on Al_2O_3 using tetrakis(ethylmethylamido) zirconium and H_2O at 285°C. These reactants deposit ZrO_2 layers that are then converted to ZrF_4 during the subsequent HF exposure. Because $Al(CH_3)_3$ does not undergo ligand-exchange with ZrF_4 [2], the ZrF_4 layer serves as an etch stop layer. QCM measurements revealed that an initial ZrO_2 thickness of just one monolayer prior to fluorination was able to stop completely the thermal Al_2O_3 ALE. Prior to reaching a ZrO_2 thickness of one monolayer, the etching inhibition was proportional to the ZrO_2 fractional coverage. The ZrF_4 etch stop layer was observed to arrest the thermal Al_2O_3 ALE for >100 ALE cycles.

The ZrF_4 etch stop layer could then be easily removed by a ligand-exchange reaction with $AlCl(CH_3)_2$ (dimethylaluminum chloride (DMAC)) [3]. The ZrF_4 etch stop layer could be applied and removed repeatedly without changing the Al_2O_3 etch rate. X-ray photoelectron spectroscopy (XPS) studies confirmed the removal of Zr on the Al_2O_3 surface after 7 cycles of DMAC and HF sequential exposures. Area selective deposition of the ZrF_4 etch stop would lead to area selective etching using HF and TMA as the reactants. Area selective deposition could be achieved based on selective reactant adsorption or substrate-dependent nucleation delays.

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AP-Contributed On Demand-19 Atomic Layer Etching of HfO_2 and ZrO_2 Landing on WS_2 Transition Metal Dichalcogenide*, Jean-Francois de Marneffe,* *D. Marinov,* imec v.z.w., Belgium*; A. Goodyear,* Oxford Instruments Plasma Technology, UK*; B. Groven,* imec v.z.w., Belgium*; P. Wyndaele,* KU Leuven, Belgium*; S. Kundu,* imec v.z.w., Belgium*; M. Cooke,* Oxford Instruments Plasma Technology, UK*; S. De Gendt,* KU Leuven, Belgium

Two-dimensional transition metal dichalcogenides (2D-TMDCs) are considered as alternative channel materials for next generation CMOS logic technology. Very large scale integration (VLSI) manufacturing requires to comply as much as possible to established processing methods and device geometries. For building VLSI compliant 2D transistor devices, the current strategy for channel gating relies on the growth of high-k oxide dielectrics (with EOT < 1nm). Electrical contacts are built by a subtractive approach where the passivating dielectric is etched away, exposing the 2D channel, then filled with the relevant metal. The present work describes the plasma etching of thin high-k dielectric stopping on WS_2, aiming at contacts fabrication. Three-layer WS_2 films were grown on SiO_2 by PEALD. After WS_2 growth, a Si nucleation layer (0.4, 0.7 or 1.0 nm, all non-continuous) was deposited using molecular beam deposition, which was oxidized by ambient exposure prior to high-k deposition. Afterwards, HfO_2 and ZrO_2 high-k dielectrics were deposited by ALD, targeting a thickness of 6 nm. Etch screening studies and process optimization were performed on HfO_2, ZrO_2 and PECVD SiO_2 films deposited directly on Si (without WS_2). The high-k films were etched in a ICP chamber, modified to enable atomic layer etching (ALE). The ALE plasma conditions used in this work were based on a continuous Ar discharge which was maintained all along the ALE cycles. The cycles were consisting of two main steps of a few seconds each, separated by purges: a short pulse (without bias) during which reactive gases were injected in the plasma (BCl_3 or Cl_2/BCl_3), followed by a biased step with only Ar. The first part of the study investigates the etch of ZrO_2 and HfO_2 using pure BCl_3 and Cl_2/BCl_3 plasmas. With pure Ar bombardment, the etch rate is zero until the bias power reaches ~ 15W. The addition of chlorine-based reactants enables etch at lower bias. Pure BCl_3 shows a non-negligible chemical etch component in the removal process. For the Cl_2/BCl_3 mixture, the etching requires a minimal bias of 5 W to proceed, indicating that the removal process is sputter enabled. The ALE synergy (at 8W bias) is calculated, giving S~53% for the pure BCl_3 discharge, while S=100% for the Cl_2/BCl_3 mixture (for both ZrO_2 and HfO_2). Applying the optimal ALE etch processes to a WS_2 films passivated with ZrO_2 or HfO_2, it is found that the high-k layers are fully removed, without major change in the composition of the underlying WS_2. The low damage high-k removal is confirmed by Raman spectroscopy, which show negligible changes after complete high-k etch.

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AP-Contributed On Demand-22 Probing the Selectivity of Area-Selective Spatial ALD + Etch-Back Supercycles for SiO_2 by Low Energy Ion Scattering, *Alfredo Mameli,* TNO-Holst Centre, Netherlands; *P. Brüner,* IONTOF GmbH, Germany; *F. Roozeboom,* TNO-Holst Centre, Netherlands; *T. Grehl,* IONTOF GmbH, Germany; *P. Poodt,* TNO-Holst Centre, Netherlands

Area-selective ALD interleaved with etch-back steps in a supercycle fashion has recently been reported as very effective in achieving high selectivity. Such supercycles can result in lower defectivity on the non-growth area and thicker layers on the growth area, as compared to solely area-selective ALD.[1, 2] The complementarity of deposition and etching techniques can therefore offer great potential for reaching the ultimate requirements in advanced device manufacturing.

Here we use low energy ion scattering (LEIS) to probe the selectivity of the first supercycle, consisting of plasma-enhanced selective spatial-ALD of SiO_2 and conventional CF_4-based reactive ion etching (RIE). Given its extreme sensitivity to the top monolayer(s) of a thin film, LEIS can reliably quantify the selectivity and defectivity on the non-growth areas in terms of surface coverage and derived thickness.

For the selective spatial ALD a three-step approach was adopted,[3] consisting of successive inhibitor, silicon precursor (BDEAS) and O_2 plasma exposures. Silicon wafers (growth area) with large ZnO patterns (non-growth area) were used as substrates. After 20 spatial ALD cycles, no silicon was detected on the non-growth area by LEIS (detection limit 2 % SiO_2 surface coverage), implying excellent process selectivity. The selectivity is however gradually lost by increasing the number of ALD cycles up to 110. On the non-growth area, the SiO_2 layers now had an averaged thickness of 3.5 nm as measured by spectroscopic ellipsometry (SE) and corroborated by LEIS measurements (86% Si surface coverage). At the same time on the growth area, a SiO_2 thickness of 11 nm was measured. In order to correct for the selectivity loss, a 3 seconds RIE step was applied, which restored the Si coverage and reduced the SiO_2 thickness on top of the non-growth area back to zero, as demonstrated by LEIS. Concurrently, 8 nm thick SiO_2 was left on the growth area.

The data presented in this work demonstrate the effectiveness of combining selective spatial ALD + etch-back corrections to achieve extreme SiO_2 selectivity while retaining high deposition rates. Furthermore, we will discuss how LEIS can provide useful information on selectivity as well as defect formation on the non-growth area. Finally, we have extended the plasma-enhanced selective spatial ALD of SiO_2 to other non-growth areas.

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AP-Contributed On Demand-25 CMOS-Compatible Processing of Atomic-Precision Donor Devices, *DeAnna Campbell, A. Leenheer, E. Anderson, S. Schmucker, J. Ivie, X. Gao, W. Lepkowski, T. Lu, L. Tracy, S. Misra,* Sandia National Laboratories

Atomic precision advanced manufacturing (APAM) is a technique for placing dopant atoms with single atomic-lattice site precision on silicon surfaces. For example, phosphorous adsorbed on a clean Si surface then capped with Si can form a monolayer (delta layer) of donors with optional selected-area patterning. The dopant atoms are incorporated into the silicon lattice through a surface-activated chemical reaction rather than a thermally activated diffusion process, **allowing for electrically active doping above the solubility limit for phosphorus in silicon**. The two-order of magnitude higher doping levels and two-dimensional nature of the dopant sheet enable new device physics and the potential for new device types and geometries.

Atomic precision fabrication requires atomically clean surfaces. Historically the APAM technique has used surface preparation techniques with high temperatures in excess of 1200 °C, but recent modifications of the surface preparation process have lowered this temperature to 800-900 °C, opening integration possibilities with CMOS. In this talk we report on the initial development of a CMOS process flow incorporating APAM doping. Based on the thermal budget and processing constraints, our basic process flow involves building the APAM device between CMOS Front-end-of-line (FEOL) and the CMOS Back-end-of-line (BEOL) steps. We will discuss possible insertion points for the APAM processing in a CMOS flow, considering possible effects on (existing) transistor channels, gate oxides, and contacts. Two additional mask layers are added, termed “APAM select” to indicate a window for APAM device processing and “APAM active” to define the actual APAM device area. We will report progress on development devices including die-level and wafer-level testing of discrete transistors and simple integrated circuits that incorporate APAM processing and wiring. We conclude with a discussion of future integration challenges such as wafer scale processing of APAM devices in a CMOS foundry flow. Direct integration of APAM components into CMOS circuits opens the door for devices with enhanced functionality.

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AP-Contributed On Demand-28 Room Temperature Operation of Donor-Based Atomically Precise Devices, *Jeffrey Ivie, L. Tracy, J. Mendez, S. Gao, E. Anderson, S. Schmucker, D. Campbell, D. Scrymgeour, A. Katzenmeyer, D. Ward, T. Lu, S. Misra,* Sandia National Laboratories

Atomic precision advanced manufacturing (APAM) of electrical devices, fabricated using hydrogen depassivation lithography in a scanning tunneling microscope, offer a way to explore device physics with the ultimate degree of control. Almost all previous work has focused on demonstrations of basic physics principles, using devices operating at cryogenic temperatures. However, these devices are isolated through freezing out leakage pathways and cannot function at room temperature, making them incompatible for large-scale integration with modern metal-oxide semiconductor (MOS) technologies. New device designs to suppress leakage pathways are critical for advancing MOS compatible APAM devices forward.

To enable room temperature operation of AP devices, we have developed a MOS compatible counter-doping scheme, which provides significant leakage current isolation around the APAM device. Refinements to the low thermal budget processes for sample preparation and epitaxial Si growth of capping material were critical for maintaining proper dopant profiles. Room temperature electrical measurements on APAM devices demonstrate electrical properties on par with devices measured at cryogenic temperatures. These electrical properties also compare well with carrier concentration and mobility extracted from room temperature spectroscopic ellipsometry measurements. This demonstration of a MOS compatible doping scheme enabling room temperature operation opens the door for integration of APAM devices with MOS technology.

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AP-Contributed On Demand-31 The Interplay of Diffusion and Size-Dependent Reactivity in Ruthenium Area-Selective Deposition, *Jan-Willem Clerix, E. Marques, A. Delabie,* KU Leuven / imec, Belgium

Area-selective deposition (ASD) is a promising technique for semiconductor device manufacturing. The replication of nanoscale patterns by ASD can simplify device fabrication process flows by reducing the number of lithography, etch and chemical-mechanical polishing steps. In addition, ASD could eliminate pattern overlay errors. In particular, Ru ASD is of interest for patterning applications as Ru hard masks with high etch resistance or for application in interconnect structures. (Ethylbenzyl)(1-ethyl-1,4-cyclohexadienyl)Ru/O_2 atomic layer deposition (ALD) has been used for Ru ASD in SiO_2/TiN nanopatterns [1]. However, undesired growth of Ru nanoparticles on the methyl-terminated SiO_2 non-growth surface limits the achievable Ru film thickness. This undesired nanoparticle growth is governed by precursor adsorption, surface diffusion of Ru adspecies and aggregation. Ru nanoparticles that are large enough (>0.85 nm) to catalyze O_2 dissociation can also grow by direct precursor adsorption on the nanoparticle.

In this study, we model how the growth mechanism influences selectivity in patterns with feature sizes of 20–200 nm. For large non-growth areas (≥100 nm wide), diffusion results in a larger amount of Ru deposited on the non-growth area than in systems without diffusion. Diffusion and aggregation result in particles, on the non-growth area, large enough (>0.85 nm) to grow by direct precursor adsorption. This direct precursor adsorption on particles is much faster than deposition on the surface. Such large particles become immobile and trapped on the non-growth surface. Conversely, for small non-growth areas (≤50 nm), diffusion of Ru adspecies from the SiO_2 non-growth surface to the TiN growth surface reduces defectivity in Ru ASD (Figure 1). These small diffusive Ru adspecies are effectively captured at the interfaces of the nanoscale patterns before their growth by precursor adsorption is catalyzed. For small non-growth areas (≤50 nm), diffusion to the growth area prevents the formation of particles larger than the critical diameter altogether.

Knowledge about the interplay of diffusion and size-dependent reactivity in nanoscale patterns can help in developing defect mitigation strategies. For instance, on small non-growth areas, regular isotropic etches should be successful in removing all defects while retaining a Ru film on the growth surface. This synergistic defectivity reduction should apply to all deposition processes with diffusion and size-dependent reactivity.

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AP-Contributed On Demand-34 Thermal Atomic Layer Etching of Nickel and Cobalt Using SO_2Cl_2 and $P(CH_3)_3$, ***Jessica Murdzek****, S. George,* University of Colorado at Boulder

Thermal atomic layer etching (ALE) is defined by sequential surface modification and volatile release reactions. Thermal metal ALE is particularly challenging because the oxidation state of the metal must be changed to match the oxidation state of the volatile metal etch product. After changing the oxidation state, the metal then needs to form a stable and volatile complex. In this work, Ni and Co ALE are developed by first changing the metal oxidation state by chlorination using SO2Cl2. Subsequently, the metal is etched by the binding of P(CH3)3 (PMe3) ligands that can volatilize the nickel or cobalt chloride.

The logic of this approach is based on the Covalent Bond Classification (CBC) method. The key is forming metal complexes that obey the “18 electron rule” or “16 electron rule”. X ligands are one-electron donors like Cl. L ligands are two-electron donors like PMe3. According to the CBC method, nickel complexes typically have NiX2L3 or NiX2L2 configurations, and cobalt complexes are typically found in the CoX2L4, CoX2L2, or CoX3L3 configurations. The goal for Ni or Co ALE is then to create these volatile metal compounds using sequential SO2Cl2 and PMe3 surface reactions. The proposed surface chemistry for Ni or Co ALE (Figure 1) assumes SO2Cl2 exposure leads to NiCl2 or CoCl2. Then the NiCl2 or CoCl2 is volatilized by binding with PMe3.

Both nickel and cobalt ALE have been studied with in situ quartz crystal microbalance (QCM). For nickel, one dose of SO2Cl2 produces a mass gain around 70 ng/cm2 at 150 °C. In comparison, for cobalt, one dose of SO2Cl2 produces a mass gain around 1,000 ng/cm2 at 150 °C (Figure 2). The large mass gain on cobalt indicates that, at the same temperature, much more CoCl2 is formed on cobalt compared with NiCl2 formed on nickel. The large surface layer of CoCl2 subsequently requires many PMe3 doses (20-30) for full removal. In comparison, only one dose of PMe3 needed to fully remove the NiCl2. According to QCM and X-Ray reflectivity (XRR) measurements, the nickel etch rate increased with increasing temperature, from 0.14 Å/cycle at 75 °C to 3.07 Å/cycle at 175 °C. Due to high levels of chlorination for cobalt, the Co etch rates are higher than the Ni etch rates at around 3-5 Å/cycle.

AP-Contributed On Demand-37 Molecular Mechanisms of Thermal Atomic Layer Etching of Cobalt, Iron, and their Alloys, ***Andrew Teplyakov,*** University of Delaware

With recent advances in sub-10 nm technologies and in developing complex supercycle etching procedures for transition metals, the molecular mechanisms of thermal atomic layer etching (ALE) are quickly coming to the forefront of the tools required to achieve atomic-level control needed for the next generation of devices. The initial attempts to assume the mechanisms of thermal dry etching based on simple chemical analysis, simplified computational models, and optimization of etching procedures have been successful in explaining some of the phenomena, including basic understanding of surface smoothing during ALE; however, utilization of realistic etching conditions, presence of multiple etchants and complex etching products, and the role of defects in surface processing require in-depth mechanistic description that is only started being developed. This presentation will focus on recent approaches that our group developed combining thermal desorption, microscopy, and surface patterning with ex-situ XPS analysis and selected computational studies to describe the molecular mechanism of thermal dry etching of cobalt, iron, and CoFeB alloy combining surface chlorination and the reactions with acetylacetonates. The same strategy can be further used to firm up our understanding of the effects of surface functionalization, defect formation, and possibly applications of combinatorial chemistry in developing modern ALE methods.

AP-Contributed On Demand-40 Towards Ultraprecise Bipolar 2D devices using Atomic Precision Advanced Manufacturing, ***James H.G. Owen****, R. Santini, E. Fuchs, J. Randall,* Zyvex Labs*; J. Mendez, X. Gao, D. Mamaluy, S. Misra,* Sandia National Laboratories

Atomic Precision Advanced Manufacturing (APAM), the ability to fabricate 2D atomic-scale devices such as the ‘single-atom transistor’ [1] and dopant patch array devices [2] via the placement of *n*-type dopants such as P and As in single planes of Si(001) has recently taken a large step forward, as the possibility of similarly placing *p*-type dopants such as B and Al has been demonstrated. While the direct equivalents of phosphine and arsine are not stable for Gr. III elements, diborane has been used to create a p-n junction[3], and for applications where few or single dopants may be required, halide precursors, BCl_3 and $AlCl_3$ are proving promising on H and Cl masks[4].

In this work, we demonstrate the ability to form bipolar atomic-scale devices using BCl_3 to place B and PH_3 to place P using a H mask. The process involves sequential patterning, dosing and incorporation steps for each dopant. We are developing the ability to produce a new class of bipolar devices with a number of advantages, including a significantly improved gain-bandwidth product, low-noise operation and cryogenic operation. An example of a npn junction device pattern after incorporation of both B and P dopants, but before burial of the complete device, is shown in Fig. 1. To help understand the operation of these 2D bipolar devices, we leverage Sandia’s open-source, TCAD (Technology Computer Aided Design) device simulator, Charon [5], and expand its capability to first understand previously published results on diborane-based 2D p-n junctions [3]. Once established, Charon modeling will be used to design device dimensions in the proposed bipolar devices.

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AP-Contributed On Demand-43 Mechanism of Thermal Dry Etching of Metallic Iron Thin Films Using Chlorine and Acetylacetone (acacH), ***Mahsa Konh****, A. Teplyakov,* University of Delaware

Thermal dry etching of metallic Iron thin films using Cl_2 and acetylacetone (acacH) was investigated. Iron metal is commonly used in magnetic random-access memory (MRAM) technology. The etching pathway was followed by detecting expected desorbing fragments during a heating ramp via temperature-programmed desorption (TPD) technique. The chemical properties of the etched surfaces were then analyzed with ex situ X-ray photoelectron spectroscopy (XPS). The morphology of the surface was studied with microscopic techniques such as scanning electron microscopy (SEM) and atomic force microscopy (AFM). To desorb volatile etch products, having an oxidized or halogenated Iron surfaces is vital, since clean surfaces resulted in decomposition of the diketone ligands. The pre-chlorination of the surfaces was shown to lead to the formation of transition metals-containing products at lower temperature compared to those on oxidized surfaces. However, halogenation makes the mechanism more complicated, and the etch product can contain both Fe^{2+} and Fe^{3+}. These products may have a combination of ligands, and their general formula can be expressed as $Fe(acac)_xCl_y$. To corroborate the formation $Fe(acac)_xCl_y$ from chlorinated iron surfaces reacting with acacH, density functional theory investigation was used. They suggest that Fe^{3+}-based fragments are more stable than those containing Fe^{2+} and that $Fe(acac)_x$ compounds were more stable compared to $Fe(acac)_xCl_y$ fragments.

AP-Contributed On Demand-46 Plasma Enhanced Atomic Layer Deposition of Molybdenum Carbonitride Films, ***Ian Campbell,*** *T. Walter, A. Molina, A. Agyapong, S. Mohney,* The Pennsylvania State University

Molybdenum nitride (MoN_y) is interesting for use in thermally stable Schottky diodes. A plasma enhanced atomic layer deposition (PEALD) process was used to prepare single-phase MoN_x films with some carbon incorporated with resistivity as low as 3×10^{-4} Ohm-cm for 33 nm thick films. The films were prepared by plasma enhanced atomic layer deposition using bis (tert-butylimino) bis (dimethylamino) molybdenum and N_2/H_2 in Ar for the plasma dose. The effects of plasma power and post-deposition annealing on electrical resistance and film composition were investigated. Increasing plasma power resulted in films with lower sheet resistance and higher N/Mo ratio. Annealing films caused a decrease in sheet resistance and N/Mo ratio. Carbon was present in the film, although in lower concentration than Mo and N, without much change for different plasma powers. This work was funded by the Office of Naval Research under Grant N000141812360.

AP-Contributed On Demand-49 Thermal Atomic Layer Etching of Al_2O_3 and Aln Using Hf or Xef_2 for Fluorination and Bcl_3 for Ligand-Exchange

***Austin Cano**, S. George,* University of Colorado at Boulder

Thermal atomic layer etching (ALE) of Al_2O_3 and AlN can be performed using HF or XeF_2 as the fluorination reactant and BCl_3 as the ligand-exchange reactant. To investigate the etching mechanism, in-situ FTIR spectroscopy was used to identify the surface species and in-situ spectroscopic ellipsometry was employed to measure the etch rates. Quadrupole mass spectrometry was also employed to identify the volatile etch products. The Al_2O_3 studies were performed using Al_2O_3 ALD films grown using trimethylaluminum (TMA) and water as the reactants. The AlN investigations were conducted using crystalline AlN to explore the etch rates. The FTIR experiments employed AlN films grown by ALD using tris(dimethylamido)aluminum and ammonia as the reactants.

When BCl_3 is used as a reactant, the ALE mechanism could occur by BCl_3 conversion of Al_2O_3 to B_2O_3 or AlN to BN. Alternatively, BCl_3 could undergo ligand-exchange with the fluorinated AlF_3 surface. For thermal Al_2O_3 ALE, FTIR studies revealed strong evidence for a conversion reaction during the initial BCl_3 exposure on Al_2O_3. The original Al-O vibrational modes were converted to B-O vibrational modes by the initial BCl_3 exposures as shown in Figure 1. After the first ALE cycle using sequential HF and BCl_3 exposures, there was no more evidence of conversion and the Al_2O_3 etching proceeded through a fluorination and ligand-exchange mechanism. Quadrupole mass spectrometry measurements observed that BCl_3 exposures to AlF_3 yielded BCl_2F and $AlCl_3$ reaction products. In situ ellipsometry measurements determined that the Al_2O_3 ALE etch rate using HF and BCl_3 as the reactants varied with temperature from 0.01 Å/cycle at 270°C to 0.19 Å/cycle at 330°C.

In-situ FTIR and spectroscopic ellipsometry were also used to explore thermal AlN ALE. FTIR studies revealed that the initial BCl_3 exposures created a thin BN layer on the surface. Subsequent HF and BCl_3 exposures were consistent with AlN fluorination by HF and subsequent F/Cl exchange to form volatile $AlCl_3$ product during BCl_3 exposures. The Al-N vibrational stretch decreased progressively versus number of HF/BCl_3 cycles as displayed in Figure 2. HF was not able to fluorinate single crystalline AlN substrates. Consequently, XeF_2 was required as a stronger fluorination source. When combining viscous flow XeF_2 exposures with static BCl_3 exposures, ellipsometry measurements showed that AlN etching occurred at temperatures above 220°C. An etch rate of 0.81 Å/cycle was obtained at 255°C. In contrast, growth of a top layer that may be composed of AlF_xCl_y was observed at lower temperatures. This top layer could be removed by long static BCl_3 exposures.

AP-Contributed On Demand-55 Mechanisms of Thermal Atomic Layer Etching (ALE) of Metal by β-diketones

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Thermal atomic layer etching (ALE) can be used for precise and damageless etching. For example, it can be used to fabricate magnetic tunnel junction (MTJ) stacks of magnetoresistive random-access memory (MRAM) devices [1]. The aim of this study is to understand the mechanisms of thermal ALE of metal in general, whose cycle consists of an oxidation step and an exposure step to b-diketones, such as; hexafluoroacetylacetone (hfacH), trifluoroacetylacetone (tfacH), and acetylacetone (acacH) molecules. For instance, thermal ALE of Ni with hfacH starts with the deprotonation of hfacH molecules after the oxidation of the Ni surface. By increasing the surface temperature in the range of 300 ~ 400 °C, volatile nickel complex $Ni(hfac)_2$ and water H_2O molecules are formed on the surface and remove the NiO layer. In this process, once a new metallic Ni surface appears, no further etching occurs, which ensures the self-liming nature of the thermal ALE process [2-5].

First, we examined the interaction of b-diketones with a metallic Ni surface, using a simulation code STATE [6,7]. It has been found that the cleavage of a C-F or C-H bond of a b-diketone is more likely to take place than the deprotonation on a metal surface. The surface roughness can also help to form C-Ni bonds, which were also observed in experiments. The reaction mechanisms that we observed in these simulations have revealed the self-limiting nature of thermal ALE for metals with b-diketone gases in general, which is consistent with earlier experimental observations [5,8].

Second, we examined the interaction of b-diketones with oxidized metal surfaces, using TURBOMOLE program [9]. It has been found that, as b-diketones approach an oxidized metal surface, they deprotonate. In this way, volatile metal complexes and H_2O molecules can be formed when b-diketone molecules interact with an oxidized metal surface. The reaction energies of such interactions have been evaluated from the simulations and we found that oxidized metal has its own desorption energy or temperature to volatilize its metal complex. Therefore, the applied temperature can be used as a self-limiting condition if the target contains different materials. In addition, hfacH is found to get more stably bonded than acacH or tfacH with an oxidized metal surface because the negatively charged F atoms in CF_3 are repelled by O atoms of the surface, which forces a deprotonated hfac to adsorb on the surface nearly vertically. This does not happen to acacH, whose CH_3 groups tend to interact directly with the metal oxide. As a result, hfacH is considered more suited for thermal ALE processes than other β-diketones.

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AP-Contributed On Demand-58 Orthogonal Bottom-up Nanopatterning of TiO_2 on SiO_2 and W on Si-H Using Thermal Atomic Layer Deposition and Etching

*S. Song, **Jungsik (Justin) Kim**, G. Parsons,* North Carolina State University

The semiconductor industry is now entering the new era of nanopatterning in manufacturing electronic device systems, and to achieve the small node size requirement, "bottom-up" processing through area selective deposition (ASD) has been considered as a key technique. Although many individual dielectric-on-dielectric (DoD) and metal-on-metal (MoM) ASD studies have shown promising results for "bottom-up" processing, no study has demonstrated coupling of different ASD processes in a sequence. Previously, our group reported a TiO_2 ALD/ALE process for TiO_2 ASD on silicon dioxide (SiO_2) vs hydrogen terminated silicon (Si-H). We also reported selective W deposition on Si-H vs SiO_2 using W ALD (SiH_4/WF_6). In this talk, we present co-compatible integration of TiO_2 ALD/ALE and W ALD for selectively patterning of TiO_2 films on SiO_2 and W films on Si-H; i.e. orthogonal TiO_2/W area selective deposition on SiO_2/Si-H line patterned substrates. The first ASD (TiO_2 ALD/ALE) selectively deposited ~18 nm TiO_2 film on SiO_2, and the subsequent ASD (W ALD) selectively deposited ~6.1 nm W film on Si-H. Between two ASDs, intermediate HF dipping was performed to regenerate hydrogen termination on Si-H to accelerate W growth on this surface. After the orthogonal process consisting of 20 TiO_2 ALD/ALE supercycles and 15 W ALD cycles, TEM results show 5.3 nm TiO_2 on SiO_2 and 6.1 nm W on Si-H. During the process, W ALD simultaneously etched TiO_2 on SiO_2 while it selectively deposited W film on Si-H. More W ALD cycles in the orthogonal process showed complete removal of TiO_2 on SiO_2 and a thicker W deposition (10 nm) on Si-H. Beyond selective deposition, the results also illustrate neighboring reaction effects near region boundaries. Our findings provide an important insight into integrating two or more selective processes including ALD, ALE, CVD, and CVE for bottom-up nanofabrication.

AP-Contributed On Demand-61 Experimental Study of Metal-Oxides Etch Selectivity*, Hamid Razavi,* University of California at Los Angeles*; M. Shen, J. Hoang, T. Lill,* Lam Research Corporation*; J. Chang,* University of California at Los Angeles

Amorphous indium gallium zinc oxide (IGZO) has been attracting attentions in thin film transistors(TFTs) research as an active semiconductor channel layer due to its high transparency, high carrier mobility, and low processing temperature. In most InGaZnO (IGZO) transistors and display cells, metal-oxide etch selectivity is crucially important during the structural patterning processes in order to realize the device fabrication.

In this work, we first discuss the wet-etch selectivity of metal-oxide thin films such as Al_2O_3, HfO_2, and InGaZnO (IGZO) using different reactive solutions. Acetylacetone ($C_5H_8O_2$), formic acid (HCOOH), and SC1 (NH_4OH/H_2O_2/DI) were examined. The metal oxide etch rates were determined by optical ellipsometry, scanning electron microscopy (SEM), and the composition of the processed surfaces was quantified by x-ray photoelectron spectroscopy. The result suggests that IGZO was etched by formic acid preferentially at ~25:1 and ~5:1 over HfO_2 and Al_2O_3, respectively.Hacac etches HfO_2 faster than Al_2O_3 or IGZO with a ratio of ~5:1.SC1 etches Al_2O_3 rapidly at a ratio of >100:1 over HfO_2 and ~20:1 over IGZO, respectively.

Next, vapor-phase etch selectivity among these oxides was investigated with formic acid and acetylacetone where the effects of pressure (100 to 250 Torr) and temperature (50 to 100°C) on the etch rate and the surface composition ratio were examined. The etch rate of IGZO processed with formic acid vapor at 80°C and 250 Torr was 7 Å/min. Using a cyclic etching process with Hacac vapor at 80°C and 250 Torr and O_2 plasma at 500 W and 30 mTorr for 1 min resulted in the etch per cycle (EPC) of 10 Å/cycle. In both methods preferential etching of ZnO was observed.

Atomic Scale Processing Focus Topic
Room On Demand - Session AP-Invited On Demand
Atomic Scale Processing Invited On Demand Session

AP-Invited On Demand-1 In-situ Characterization of the Earliest Stages of Selective ALD Growth and Inhibition*, Alex Martinson,* Argonne National Laboratory **INVITED**

A vast literature of ALD synthesis and processing has been developed to produce high quality thin films with compositions that span the periodic table. However, these synthesis and processing conditions are often optimized for *adding thickness* to growing film front via $(A\text{-}B)_n$ cycles. Our associated mechanistic understanding of these processes is often gleaned from in situ study of film growth, which can be examined in detail and averaged over many sequential and identical cycles. In contrast, the earliest stages of nucleation, inhibition, and selective ALD may differ significantly with each cycle and add material with far sub-monolayer coverage. This makes characterizing and understanding nucleation, inhibition, and selective growth especially challenging. I will describe our recent efforts to understand nucleation and inhibition on a variety of substrates including self-assembled monolayers (SAMs) and graphene. A combination of in situ quartz crystal microbalance, spectroscopic ellipsometry, ab initio computation, and microcalorimetry reveal new insight into the earliest stages of deposition.

AP-Invited On Demand-7 Atomic Layer Processing Using Low-Energy Cluster Beam Irradiation*, Noriaki Toyoda,* University of Hyogo, Japan*; K. Uematsu,* University of Hyogo, Japan, Afghanistan **INVITED**

Gas cluster ion beams (GCIBs) are clusters of several thousands of gaseous atoms or molecules. Since thousands of low-energy (several eV) molecules bombard the same position simultaneously, bombarded area experiences transient high-temperature and high-pressure conditions. These phenomena enhance surface reactions, and also enhances desorption of etching products.

We have been studying atomic layer etching using low-energy GCIB to enhance the surface reactions between adsorbed molecules and target atoms.

In this study, we report the surface reactions between metals (such as Ni) and diketone molecules induced by Ar or O2-GCIB irradiation. From the in-situ XPS studies, the nickel oxide layer with acac or hfac adsorption are selectively removed by 5 keV Ar-GCIB irradiation. After removal of the nickel oxide, metallic nickel surface appeared, and etching stopped. From the etching depth measurement after multi-cycle ALE of Ni films, it also showed that both oxidation of nickel and adsorption of acac were necessary for Ni ALE with GCIB. In this report, preliminary results of etching of MoS2 using GCIB will be also reported.

AP-Invited On Demand-13 The Thinner, The Better - Characterization of Ultra-thin Films by Low Energy Ion Scattering (LEIS)*, Thomas Grehl,* *P. Brüner,* 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 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 Angstroms. This allows to study the development of the film thickness while also monitoring the film closure to determine the growth mode.

In some cases, low energy noble gas sputtering can 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.

AP-Invited On Demand-19 Spectroscopic Ellipsometry for Atomic Scale Processing*, Harm Knoops,* Oxford Instruments Plasma Technology, Netherlands **INVITED**

To develop, improve and understand atomic scale processing techniques such as atomic layer deposition (ALD) and atomic layer etching (ALE) it is important to have sensitive techniques to characterize thin material increases, decreases or property changes. Spectroscopic ellipsometry (SE) is excellent for this purpose since it is a non-invasive all-optical diagnostic which can relatively easily monitor changes in thickness ranging from 0.1 to 100 nm.[1] This talk will discuss the relevant basics of SE and will use examples to illustrate why SE it is well suited for atomic scale processing now and in the future. Key characteristics of ALD and ALE are self-limiting behavior and synergy (needing both reaction steps to take place). Using ex situ analysis of thick films to study these aspects is cumbersome, while with in situ SE there are many examples of easy characterization. Furthermore, initial growth effects relevant in ALD and area-selective ALD are best studied in situ.

For ALD, highlighted examples will include studying saturation, which can provide evidence for important processes such as the redeposition effect for silicon nitride ALD,[2] and studying saturation is even possible for 2D materials which are challenging to model by SE. When using ex situ SE and data by other diagnostics (e.g. electrical and infrared) a deeper investigation of material properties is possible. For instance electrical properties can be calculated from the Drude absorption yielding insight into the electrical resistivity and electron scattering effects in ultrathin ZnO films.[3] For ALE, SE has been much less used than for ALD, but similarly there are great opportunities and examples there. Easiest analysis occurs when smooth films of the target material are available (or deposited) on substrates. To this end the synergy of ALE has been tested and confirmed for ALE of ZnO using Hacac and O_2 plasma.[4] But also recently for ALE of Al_2O_3 using $AlMe_3$ and SF_6.[5] Note that the latter chemistry can also result in the ALD of AlF_3 and SE is a powerful tool to determine in situ whether ALD or ALE is occurring and under which circumstances. By clever set up and utilization of this diagnostic, SE has become a powerful and often essential tool to develop and understand ALD and ALE processes.

[1] Langereis et al., J. Phys. D: Appl. Phys. 42, 073001 (2009)

[2] Knoops et al., APL 107, 014102 (2015)

[3] Knoops et al., JVST A 33, 021509 (2015)

[4] Mameli et al., ACS Appl. Mater. Interfaces 10, 38588 (2018)

[5] Chittock et al., *In preparation*

AP-Invited On Demand-25 Area-selective Atomic Layer Deposition of Palladium and Atomic Layer Etching of Palladium*, H. Nallan, X. Yang, B. Coffey,* ***John Ekerdt,*** University of Texas at Austin **INVITED**

ALD of metals can suffer from long nucleation delays leading to unwanted growth outside the patterned regions.We present an approach that first deposits a metal oxide selectively and reduces this metal oxide to the metal.This metal then serves as the nucleation site for ALD of Pd using a precursor chemistry that requires activation of molecular hydrogen.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 – the issue is controlled oxidation while minimizing damage to adjacent surfaces.We present a low temperature route that involves VUV activation of O2 to produce atomic oxygen and ozone, with atomic oxygen being the dominant species that oxidizes the near surface region of Pd.Oxidation extents differ between continuous films and discontinuous films enabling the removal of metal islands without significantly etching the film.

This talk will discuss patterning an oxide substrate using UV-crosslinked 40-nm polystyrene (PS) films; the uncrosslinked PS is dissolved with toluene to expose the oxide surface. The ALD of NiO is highly selective on the exposed oxide surface using bis(N,N'-di-tert-butylacetamidinato)nickel(II) and H2O as coreactants. Ni and partially reduced NiO(1-x) are generated using molecular hydrogen and/or atomic hydrogen to present a surface that dissociates H2 and enables Pd ALD with Pd(hfac)2 and H2 to proceed with little to no nucleation delay. Finally, the talk will discuss vacuum ultraviolet (115 nm < λ < 400 nm) enhanced atomic layer etching (ALE) of thin (~2 and 20 nm) Pd films at 100 °C using formic acid as the etchant. Density functional theory is used to study the adsorption of oxidants (O and O3) and nudged elastic band calculations describe O diffusion into the films to understand the kinetic limitations of the oxidation step. Low-temperature Pd oxidation at 100 °C is achieved by exposure to vacuum ultraviolet (VUV) light (λ<160 nm) in the presence of O2. The islands are completely oxidized while Pd oxidation of a film is limited to approximately one atomic layer. Any PdO that forms is etched by exposure to formic acid.

AP-Invited On Demand-31 Strategies for a Selective Deposition Process Combining Deposition and Etching Steps in a Unique Tool*,* ***Christophe Vallée,*** SUNY POLY, Albany*; M. Bonvalot, T. Yeghoyan, R. Vallat, M. Jaffal, V. Pesce,* LTM - UGA/CNRS, France*; A. Chaker,* University of Manchester, UK*; S. Belahcen, G. Lefevre, B. Pelissier,* LTM - UGA/CNRS, France*; N. Posséme, R. Gassilloud,* CEA/LETI-University Grenoble Alpes, France **INVITED**

Selective deposition by ALD can be obtained using: inherent selectivity of the process[1-2], surface activation[3], surface deactivation [4-5], and ABC typesuper-cycles [6]. The strategy developed in our laboratory is based on super-cycles with alternate deposition and etching steps[7-10] in a unique ALD tool.

Up to now, we have developed ASD processes with many different types of etching steps, such as high-pressure plasma etching (radicals only), Reactive Ion etching, Atomic layer etching or sputtering (physical) etching steps. For this purpose, two different PEALD tools are used: either a CCP capacitive discharge tool from Kobus (now Plasma-Therm) with a grounded substrate holder, or an ICP PEALD tool from Oxford (Flexal) with an additional RF biasing of the substrate.

Plasmas from the PEALD tool can also be developed to the benefit for ASD processes. For instance, an appropriate plasma chemistry can modify the nucleation delay. Moreover, thanks to substrate biasing, one can also take advantage of energetic ions from the plasma to locally modify the nucleation delay as well as the materials GPC or density. This latest route combined with a post-deposition etching process is a fast and easy to develop process for topographically selective deposition (deposition in one space direction only).

This presentation will outline and provide several examples of all these different scenarios that we have developed recently in our group, as well as state of the art ASD solutions from other groups using etching steps or ions in PEALD processes.

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[3] A.J. M. Mackus *et al,* Chem. Mater. **24,** 1752 (2012)

[4] M. Fang and J.C. Ho, ACS Nano **9**, 8651 (2015)

[5] E. Farm *et al*, Sci. Tech. **27**, 074004 (2012)

[6] A. Mameli *et al*, ACS Nano **11,** 9303 (2017)

[7] R. Vallat *et al*, J. Vac. Sci. Technol. A **35**, 01B104 (2016)

[8] R. Vallat *et al*, J. Vac. Sci. Technol. A **37**, 020918 (2019)

[9] A. Chaker *et al*, Appl. Phys. Lett. **114**, 043101 (2019)

[10] C. Vallée *et al*, J. Vac. Sci. Technol. A **38**, 033007 (2020)

AP-Invited On Demand-37 Thermal Atomic Layer Etching - An Emerging and Enabling Etching Technology*,* ***Andreas Fischer****, A. Routzahn, R. Gasvoda, P. Lemaire, J. Sims, T. Lill,* Lam Research Corporation **INVITED**

In this presentation we discuss the state-of-the-art status of thermal atomic layer etching of various materials such as metals, metal oxides, metal nitrides, semiconductors and their oxides.We outline the basic chemical and thermodynamic reaction principles and identify materials relevant to the semiconductor industry that lend themselves for isotropic atomic layer etching.

Furthermore, application examples of this new etch technology are illustrated on device structures and its benefits as well as challenges are examined.We give an example of the technical challenges related to high aspect-ratio atomic layer etching including an overview on how to mitigate it in modern 3D NAND test structures.

Finally, we provide an outlook of the role thermal ALE can play in the manufacturing of advanced semiconductor devices.

AP-Invited On Demand-43 Nanoscale Chemical Analysis and Mapping of Atomic Scale Processes via Photo-Induced Force Microscopy*,* ***Sung Park,*** *D. Nowak, T. Albrecht,* Molecular Vista **INVITED**

As device feature sizes move beyond 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. Atomic scale thicknesses, nanoscale lateral dimensions, and the combination of multiple materials consisting of organic and inorganic compounds, metals, and 1D/2D materials demand new metrology and characterization techniques to be developed to adequately asses 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-10 nm spatial resolution). The spectroscopic capability is useful for ascertaining the quality of the molecular species while the mapping capability is useful for investigating 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 scale processes will be presented.

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Applied Surface Science Division
Room On Demand - Session AS-Contributed On Demand
Applied Surface Science Contributed On Demand Session

AS-Contributed On Demand-1 Peeling the Onion: Argon Cluster Sputtering Reveals the Internal Distribution of Species in Organic Nanoparticles*, Y. Pei, J. Vorng, R. Havelund, D. Cant,* ***Alexander Shard,*** National Physical Laboratory, UK

Ideally, we would like to get detailed structural information from nanoparticles and sub-micrometre particles by removing each layer of material and analysing the freshly exposed surface, like peeling an onion. Trying to do this using traditional surface analysis methods is difficult enough to make anyone cry, also like peeling an onion. However, if we could approach this, the quantitative power and molecular specificity of XPS and SIMS would be invaluable to the development of functional organic particles, such as those used in drug delivery and diagnostic applications. By sputtering monodisperse sub-micrometre polystyrene particles with an argon cluster ion beam we demonstrate that their shape can be usefully modelled using a constant, angle-independent sputtering yield. This permits the development of a model to analyse XPS and SIMS data from surfaces coated with multilayers of monodisperse PTFE-PMMA core-shell particles. In this work, the SIMS data shows clear peaks for the fluorinated core signal from at least three layers of the packed particles, demonstrating potentially useful information. The XPS data from the first layer of particles can be analysed using our model to establish the diameter of the core which agrees, to within 6%, with SEM measurements of the uncoated core. Furthermore, the internal distribution of PTFE agrees with the expected distribution of internal core locations, which is an equally weighted random distribution, with no part of the core closer than ~10 nm of the surface. Whilst the SIMS data is potentially more useful for material identification, it implies a core diameter 40% smaller than expected and more closely located at the centre of the particle. We show that this discrepancy is most likely due to a SIMS matrix effect in which PMMA suppresses the generation of positive secondary ions from PTFE.

AS-Contributed On Demand-4 Buried Interface and Buried Film Analysis Using Lab-Scale Haxpes Instruments*, **Thierry Conard**, C. Zborowski, A. Vanleenhove, I. Hoflijk, I. Vaesen, P. van der Heide,* IMEC, Belgium

Nanotechnology is playing a fundamental role in the improvement of our life conditions. Progress in various domains such as microelectronics, storing and producing energy (batteries, solar cells, ...) and life sciences is very often linked to the improvement of our knowledge about interactions at material interfaces. Photoemission has a major role in the characterization of surfaces and interfaces thanks to its wide availability in laboratories all over the world. However, traditionally, the photon energy is limited since standard photoemission lab-tools were equipped with soft X-ray Mg Kα or AlKα radiation (~1.5 keV), which makes the analysis of buried interfaces deeper than a few nanometers impossible without the use of destructive profiling methods (sputtering), leading to strong chemical modification of the layers/interfaces analyzed.

Unfortunately, in many modern technologies, deeper interfaces need to be analyzed. This can be done by increasing the photon energy. However, until recently, this has seldomly been applied as it required synchrotron radiation, which was only available in specialized synchrotron facilities with limited access while process development usually requires a fast feedback loop and routine measurements. However, the recent development of several lab-scale instruments including high photon energy monochromatized sources (Ag Kα ~2.9keV, Cr Kα ~5.4 keV or Ga Kα ~9.25 keV)opened the possibility of non-destructive buried interface analysis for process development work.

In this presentation, we will demonstrate the possibilities of the HAXPES lab-scale systems from Physical Electronics (PHI*Quantes*, using Cr Kαphotons) and ScientaOmicron (*HAXPES-lab*, using for Ga Kα photons) for two different applications. First, we will look into the chemical analysis of interfaces in multi-layer high-k/metal gate stacks (such as $TiN/HfO_2/SiO_2Si$) and investigate the modifications of the layer chemistry of the buried layers upon thermal treatments. One of the difficulties in using concomitantly Al Ka-based and high-energy photoemission is achieving coherent quantification. Therefore, the second part of the presentation will describe an approach by which the necessary sensitivity factors are determined. The resulting quantification accuracy will be demonstrated by a quantitative analysis of the composition of binary and ternary materials (such as InAs, InGaAs, InGaZnO, ...).

AS-Contributed On Demand-7 ***Non-Destructive Chemical Characterization and Thickness Determination of Layer Stacks by Laboratory-Based Hard X-Ray Photoelectron Spectroscopy*** ***, Anja Vanleenhove****, T. Conard, C. Zborowski, I. Hoflijk, P. van der Heide,* IMEC, Belgium*; K. Artyushkova, D. Watson,* Physical Electronics USA

XPS is widely used for non-destructive analysis of the chemical composition of thin layers and interfaces. In its angle-resolved mode, it can be used for the determination of composition depth profiles and layer thicknesses. With the commonly used soft X-ray laboratory instrument, the analysis is limited to the top 5-10nm. The recent development of laboratory-based hard X-ray photoelectron spectroscopy with an X-ray energy higher than 5keV opens the opportunity to examine layers and interfaces buried up to 20nm and deeper in a non-destructive way. To evaluate the application of lab-based HAXPES for thickness and composition determination, various multilayer samples with total thicknesses up to 20nm are examined by HAXPES and soft X-ray XPS. All experiments are performed in a PHI Quantes system equipped with two monochromatic X-ray sources, Al Kα (1486.6eV) and Cr Kα (5414.7eV), hence combining both XPS and HAXPES in one instrument.

Both angle resolved and angle integrated data analysis options are discussed. In the first part, we discuss the analysis of angle resolved data, resulting in relative depth profiles and thickness information, which is performed with the MultiPak and StrataPHI software. The latter is recently developed by Physical Electronics, USA. We discuss the analysis with regard to instrumental parameters and the physical parameters (attenuation lengths, sensitivity factors, etc.) necessary for the calculations. In a second part, we demonstrate how the analysis of angle integrated spectra can provide identical information by combining XPS and HAXPES data, thus eliminating the need to perform time-consuming angle resolved measurements.

The samples considered in this study – multilayer Al_2O_3 and HfO_2, SiO_2, Si_3N_4, ZrO_2, ZnO, Lu_2O_3, TiN – originated from semiconductor processing. The thin film multilayer stacks, which are within the range of both XPS and HAXPES sampling depth, are examined both by XPS and HAXPES. The results are validated by HAADF-STEM and EDS analysis. The thicker stacks are used to demonstrate the specific interest of HAXPES for increased depth-information capabilities.

AS-Contributed On Demand-10 Temperature Dependent Changes in Surface Chemistry of $SrTiO_3$ Analysed With XPS, Cluster Depth Profiling and Ion Scattering Spectroscopy*, **Paul Mack**,* Thermo Fisher Scientific, UK

Small cluster (Ar_{300}^+) depth profiling of a $SrTiO_3$ thin film has previously been demonstrated.Compared to low energy (500eV) monatomic argon sputtering, the cluster depth profiling caused much lower chemical damage, with a more realistic [Sr]:[Ti] stoichiometry observed throughout the profile and lower chemical damage to the Ti^{4+} oxidation state.$SrTiO_3$ is of interest because it has potential use in energy storage or photocatalysis and if future devices performance is to be optimized, it is necessary to accurately measure film compostion/chemistry and also to understand how these may change when the devices are exposed to changes in local conditions, such as temperature.

In an extension to previous work, a $SrTiO_3$ sample has been analysed with XPS cluster depth profiling over a range of temperatures (from room temperature to >600°C).One of the aims of the work is detect reduction of the Ti^{4+} oxidation state to Ti^{3+}, caused by changes in temperature.The chemical shift in the Ti2p region is reasonably large (~2eV), but the relative concentration of any Ti^{3+} formed can be quite low.Distinguishing the Ti^{3+} from the Ti^{4+} therefore requites the XPS system to have very high sensitivity and good charge compensation.

Additionally, ion scattering spectroscopy (ISS) was used to evaluate the termination of the $SrTiO_3$ film as a function of temperature.ISS is even more surface sensitive than XPS and is the ideal analytical technique for measuring if there are local changes in the top monolayer of the $SrTiO_3$, e.g. -TiO_2 termination.Combination of small argon cluster profiling with both XPS and ISS gives a more comprehensive characterization of the $SrTiO_3$ than is possible with just a single analytical technique.

AS-Contributed On Demand-13 $LiTaO_3$(110) Nano-Bonding with Si-based Materials via Surface Energy Engineering (SEE) and Three Liquid Contact Angle Analysis (3LCAA)*, **Shefali Prakash**, A. Elison, S. Swaminathan, M. Sahal,* Arizona State University*; B. Baker, J. Kintz,* Intel Corporation*; A. Yano,* Texas A&M University*; S. Narayan,* University of Pennsylvania*; A. Brimhall,* Micron Technology*; L. Puglisi, R. Culbertson, N. Herbots,* Arizona State University

Integrating piezo-electrics to Si can be achieved by Direct Wafer Bonding (DWB) for materials with large mismatch in lattice constant and/or Coefficients of Thermal Expansion (CTE).

DWB by Nano-Bonding^{TM} uses SEE instead of high temperature is a logical choice for bonding $LiTaO_3$ to Si and SiO_2, since the CTE of $LiTaO_3$(110), ~18.3 × 10^{-6}/K, is mismatched to Si by a factor 8, and to α-quartz SiO_2, (α-q SiO_2) by a factor 25. Moreover, at 500 K, $LiTaO_3$ decomposes into Ta_2O_5 and Li.

Surface Energy Engineering (SEE) for Nano-Bonding^{TM1} modifies the Surface Energy, γ^T, and hydro-affinity, HA, to far-from-equilibrium states, in air, planarizes at the nano-, micro- and macro-scale, and nucleates *2D-Precursor Phases*, in synergy for both materials. 2D precursor phases act as catalysts when in contact, forming a cross-bonded, solid *interphase*. To engineer γ^T and HA, the initial γ^T of as received wafers is computed from the Lifshitz-van der Waals' interaction energy, γ^{LW}, acceptors energy, γ^-, and donors energy, γ^+, measured using Three Liquid Contact Angle Analysis and the van Oss–Chaudhury–Good theory.

B-doped p^--Si(100) is uniformly hydrophilic with a water contact angle θ_{H20} of 37.7 ± 0.6°[2]. 6" α-q SiO_2(100) is uniformly hydrophilic, with a θ_{H20} of 65.5 ± 0.6°. $LiTaO_3$(110) is mostly hydrophobic, with an average θ_{H20} of 49.4 ± 6.6°, and poor uniformity across 6"[3]. Hydrophilic α-q SiO_2(100) γ^T averages 48.7 ± 1.5 mJ/m^2. γ^T averages 40.8 ± 2 mJ/m^2 for $LiTaO_3$ (110), and 53 ± 0.2 mJ/m^2 for Si(100).

The ΔG of interaction for $LiTaO_3$ (110) with Si(100) is -8.18 mJ/m^2 and -0.46 mJ/m^2 with α-q SiO_2, at RT in atmosphere and HR = 25%. The negative signs of ΔG reveal that spontaneous bonding between $LiTaO_3$(110), and Si(100) and α-q SiO_2(100) is energetically favored.

Hence, $LiTaO_3$(110) and Si(100) could spontaneously nano-bond when nano-contacted at RT, which is in fact observed experimentally[2]. SEE can lower the ΔG to enhance the kinetics of Nano-Bonding™ interphase formation and bonding strength. Ab-Initio Molecular Dynamics (MD) simulations of $LiTaO_3$(110) Surface Density of State (DOS) simulation using CrystalMaker® for $LiTaO_3$(110) in contact with Si(100) before and after SEE can yield insights into the engineering of ΔG, by correlating computed modified surface charges, maximized dipole moments, electronic configuration to the measured γ^T.

[1] US & Int. Pat. 6,613,677; 7,851,365;9,018,077;9,589,801 (2017)

[2] Baker, B. *et al*.,J. of Vac.Sci& Techn.A37, no. 4 (2019): 041101

[3] Sahal, M.*et al*. Bull.of the APS 64 (2019)

AS-Contributed On Demand-16 Understanding *Interphase* Formation in Nano-Bonding™ Of Gaas to Si in Air at T ≤ 220°C via Surface Energy Engineering Based on 3lCAA, IBA, XPS, SAM and TEM, *A. Gurijala, N. Suresh, A. Chow, S. Khanna, M. Sahal,* Arizona State University Physics Department*; S. Ram,* Yale University*; T. Diaz, M. Bertram, C. Cornejo, W. Peng, T. Balasooriya, T. Karcher,* Arizona State University Physics Department*; R. Culbertson,* Arizona State University Physics Department*; K. Kavanaugh,* Simon Fraser University, Canada*; N. Herbots,* Arizona State University Physics Department*; **Pranav Penmatcha**, S. Jandhyala,* Arizona State University

Si and GaAs absorb the solar spectrum between 0.4 -1.1 µm and 0.8 - 2 µm with a PV Conversion Efficiency (PVCE) ~ 24%, and ~ 35 %, respectively. Integrating GaAs to Si yields more efficient tandem cells. However, their PVCE reaches presently only ~ 33 %[1].

DWB by Nano-Bonding™[1-3](NB) in air uses Surface Energy Engineering (SEE) to remove native oxide, shift surface energies, γ^T, and hydro-affinity (H-A) far-from-equilibrium, planarize surfaces by reducing warp and roughness, and form *2D Precursor Phases*[2-4](2D-PP) to catalyze molecular cross-bonds via electron exchange. NB activates 2DPP to form a cross-bonding *interphase* under 35-60 kPA and/or gas pressurization. 2DPP formation is described in [2].

$\gamma^T$and H-A are measured by Three Liquid Contact Angle Analysis to ± 1 mJ./m^2 from contact angles for water, glycerin, and α-bromonaphthalene. Ion Beam Analysis via nuclear resonance with channeling measures O coverage to ± 0.2 - 0.5 ML. X-Ray Photoelectron Spectroscopy analyzes composition and bonding.

As-received (AR) Te-doped n+-GaAs is hydrophobic, with γ^T = 33 ± 1 mJ/m^2. After SEE, GaAs becomes *super-hydrophilic*with γ^Tdoubling to 66 ±1 mJ/m^2. Meanwhile, AR B-doped p^--Si[3-4] is initially hydrophilic with γ^T = 53 ± 1mJ/m^2, and becomes hydrophobic after SEE with γ^T = 48 ± 3 mJ/m^2. Absolute Oxygen coverage decreases on n+-GaAs from 7.2 ± 0.5 ML to 3.6 ± 0.2 ML, and from 13.3 ± 0.5 ML to 11.8 ± 0.5 ML on Si p^--Si .

The $As_2O_5$to As_2O_3 ratio decreases by a factor 2. So the same amount of As is bound to Oxygen, but to three O rather than five.

The GaAs to Ga_2O_3 ratio remains 6:4. Adventitious C affects XPS data by < 10% with a correlation factor < 0.6.

SEE reverses hydro-affinity of Si and GaAs without affecting the Ga:As ratio.

The GaAs/Si interface is imaged by Surface Acoustic wave Microscopy (SAM) and cross-section TEM. 98% of the compressed GaAs area to Si is found bonded, when using 40 kPa and steam pressurization. In addition, the cross-bonding is found to extend beyond the compressed area into the regions around it where mechanical compression is not applied. The additional surface area found to be bonded can reach up to 8 times the compressed area.

The reaction rate is estimated from X-TEM. Key parameters to maximize bonding, and the mechanism of cross-bonding *interphase* formation during NB of GaAs to Si in air are derived from experiments varying SEE and NB conditions and will be discussed.

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AS-Contributed On Demand-19 Computed Surface Vibration Modes, IR Absorption and Gibbs Free Energy for LiTaO3(110) and LiNbO3(110) Correlation with Surface Energies Measured via 3LCAA*, **Mohammed Sahal**, A. Elison, S. Prakash, S. Swaminathan, R. Rane, L. Puglisi, B. Baker, R. Culbertson, N. Herbots,* Arizona State University

Piezoelectric $LiTaO_3$(LT) and $LiNbO_3$(LN) monolithic integration to Si has the potential to deliver IC's with infrared and acoustic sensing capabilities.

The lattice mismatch of LT(110) and LN(110) with Si(100) is almost identical, ~ 34%, and ~ 48% with α-q SiO_2(100). Such large mismatch limits hetero-epitaxy of relaxed LT and LN on Si. Moreover, deposition involving multiple buffer interface layers is difficult due to thermal instability of both LT and LN above 500K, which decomposes into Ta or Nb oxides while Li^+ out-diffuses.

Nano-Bonding™(NB[4]), a Direct Wafer Bonding (DWB) process carried out in a Class 10/ISO 4 environment aims to form molecular cross-bonds at the interface of two distinct wafers via a distinct ordered inter-phase[1,2] Room Temperature NB uses Surface Energy Engineering (SEE) to eliminate three key issues with DWB and hetero-epitaxy: lattice mismatch, Coefficient of Thermal Expansion mismatch and thermal instability.

SEE modifies the initial equilibrium state of surfaces into a metastable 'far-from- equilibrium' state via nano-scale planarization, and causes the nucleation of 2D-Precursor Phases[3,4,5]. 2D-PP can be activated at room temperature by gas and mechanical pressurization to form molecular cross-bonds. Design of SEE for a material pair involves surface energy γ and hydro-affinity H-A measurement via Three Liquid Contact Angle Analysis (3LCAA) using the van-Oss-Chaudhury-Good theory followed by γ modification of 6'' wafer surface into a 'far-from-equilibrium' meta-stable state.

In this work, γ components and ΔG_{H20} measured on 'As Received' (AR) LT(110), LN(110), α-q SiO_2(100) and Si(100) are inter-compared with their computed IR absorption spectra, Surface Electron Density of States(SE-DOS) simulated by Crystal Maker®.

The highest IR Spectrum Intensity Peaks(IRS-IP)was observed for α-q SiO_2(100) with a wavenumber of 1330 cm^{-1} with a Polar Surface Energy (PSE) value as 14 ± 1.3 mJ/m^2. Similarly, IRS-IP for LT(110), LN(110) and Si(100) were 1014 cm^{-1}, 1278 cm^{-1} and 489 cm^{-1} and their PSE contributions were 4.7 ± 0.2 mJ/m^2, 7.5 ± 2.1 mJ/m^2 and 5 ± 0.4 mJ/m^2 respectively. IRS-IP simulated on each wafer STL were representative of their respective PSE contributions since PSE contributions decreases with higher order of surface symmetry. It should be noted that the PSE of LT(110) is slightly lower than Si(100), which could be due the presence of Si(100) native oxide. Wafers having IRS-IPs, PSE contributions had least symmetric SE-DOS as expected. These results lay the foundation to correlate and predict the macro-thermodynamic γ components and Gibbs free energy change with their atomistic models and simulations.

AS-Contributed On Demand-22 Quantitative Fabric Analysis of Clay Flocs Using Two-Dimensional X-Ray Diffraction*, **Tao Jiang**, G. Zhang,* UMass Amherst

Clay flocs, by definition, are groups of clay particles associated primarily with face-to-face association to form structural units in clays via small-scale surface/interfacial forces. Owing to the widespread presence of clay minerals in the terrestrial and marine environments, understanding the microstructural characteristics of clay flocs is crucial in many environmental process and industrial applications. In this study, two-dimensional X-ray diffraction technique was employed to yield quantitative analysis of clay flocs. A group of pure kaolinite flocs with concentration of 1 g/l were first absorbed into a Kapton tube, and then subjected to the transmission of X-ray generated at MIT X-ray diffraction shared experimental facility. After multiple frames of scanning with varying tilt and rotation angles, pole figure that represent the stereographic projection of the orientation of crystal planes. The results indicate that the kaolinite floc group has random particle orientation when no external load is applied.

AS-Contributed On Demand-25 Deep Depth profiling using Gas Cluster SIMS – Micrometer Topography Development and Effects on Depth Resolution*, Shin Muramoto,* NIST*; D. Graham,* University of Washington

Secondary ion mass spectrometry using the argon cluster primary ion beam enables molecular compositional depth profiling of organic thin films with minimal loss of chemical information or changes in sputter rate. However, for depth profiles of thicker organic films (> 10 µm of sputtered depth) we have observed the rapid formation of micron-scale topography in the shape of pillars that significantly affect both the linearity of the sputter yield and depth resolution. For example, sputtering of gelatin using an ion dose of 7 x 10^{16} ions/cm^2 resulted in the formation of 42 µm deep craters with 20 µm tall pillars on the crater bottom, pointed at 45° towards the gas cluster source. When the pillars reached a threshold number on the crater bottom, the sputter yield of gelatin was also seen to change, eventually stopping the sputtering. In addition, by using 40 µm polystyrene spheres embedded in gelatin, it was possible to measure the depth resolution at the film-sphere interface as a function of sputtered depth and observe when possible distortions in the 3D image occurred due to changes in the sputter rate. To minimize this distortion, a step-wise, staggered sample rotation was employed. This minimized the formation of micro-pillars on the crater bottom by changing the direction of the beam, allowing the pillars to be sputtered away and minimizing their growth. In this way, it was possible to minimize distortions in the 3D image of the embedded spheres. The depth resolutions were seen to improve from (9.4 ± 3.2) µm to (7.1 ± 1.6) µm. Using these numbers, it was possible to quantitatively measure the effect of micron-scale topography and sample rotation on the quality of the depth profile.

AS-Contributed On Demand-28 Effects of Li Deintercalation in the Electronic Structure of Li_xCoO_2 Epitaxial Thin Films*, Elena Salagre,* Dto. Fisica Materia Condensada, Univ Autonoma de Madrid, Spain*; P. Segovia,* Univ Autonoma de Madrid, IFIMAC, Spain*; M. González-Barrio,* Univ. Complutense de Madrid, Spain*; J. Pearson,* University of Maryland*; I. Takeuchi,* University of Maryland*; E. Fuller, A. Talin,* Sandia National Laboratories*; M. Jugovac, P. Moras,* Istituto di Struttura della Materia, Consiglio Nazionale delle Ricerche, Italy*; A. Mascaraque,* Dto. Física de Materiales, Fac. Ciencias Físicas, Univ. Complutense de Madrid, Spain*; E. Garcia-Michel,* Univ. Autonoma de Madrid, IFIMAC , Spain

$LiCoO_2$ (LCO) is one of the most common cathode material in rechargeable Li-ion batteries, mainly due to its high-energy capacity and good cyclability [1]. This material undergoes a complex, and not yet fully understood, set of phase transitions during Li deintercalation that plays a key role on battery performance and degradation. Stoichiometric LCO (x=1) is an insulator, but upon Li removal of 0.5% (x=0.95) it undergoes an insulator to metal transition of yet unclear origin and interpretation (Mott vs. Anderson type)[2,3]. The metallic phase has the same crystalline structure (R-3m) as the insulating one, however it has slightly different lattice parameters. These two hexagonal phases coexist in the range 0.95<x<0.75 [4]. The formation of the metallic phase is explained by hole doping of the Co t_{2g} band [5] after Li deintercalation, but the modifications experienced by the electronic structure are still controversial [2,3].

In this work we analyze high-quality epitaxial thin films of LCO grown by pulsed laser deposition on Nb-doped $SrTiO_3$(111). We perform high resolution ARPES, XPS and XAS, using synchrotron light, to characterize the electronic properties of LCO for different Li molar fraction values (x). The changes in the electronic structure during the metal-insulator transition are observed under ultra high vacuum conditions and the quality of the surface has been verified thoroughly throughout the process. We obtain detailed Fermi surfaces and constant energy surfaces, as well as band dispersion maps for the discharged (x=1) and partially charged (x<1) LCO epitaxial films. Information about the chemical and structural changes is obtained from high-resolution Co 3p, Li 1s and O 1s core levels and from the Co L and O K absorption edges.

The expected formation of Co^{4+} and of oxygen holes related to the metallization, are studied in the context of the partial hybridization of Co 3d and O 2p orbitals. We report the formation of a hole-like metallic band and measure the effective mass of the carriers, before and after Li deintercalation. A change in the band dispersion and a reorganization of spectral weights at the Fermi surface is also described for large hole doping levels. We present results that clarify the controversial topics regarding the metallization and charge compensation during Li deintercalation[4].

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AS-Contributed On Demand-31 Understanding the Effect of Surface Treatment on the Boehmite Scale Formation on Aluminum 6061*, Lyndi Strange,* *X. Yu, V. Shutthanandan, J. Gao, J. Son, Y. Zhang, R. Prabhakaran, K. Brooks, V. Joshi,* Pacific Northwest National Laboratory

Low-enriched uranium (LEU) alloyed with 10 wt% molybdenum (U-10Mo) has been identified as a promising alternative to high-enriched uranium (HEU) for the United States High Performance Research Reactors. The nominal configuration of the U-10Mo plate-type fuel is a metallic U-10Mo fuel foil with a very thin Zr diffusion interlayer barrier clad with aluminum alloy 6061 (Al 6061). The surface of the aluminum cladding is coated with a boehmite layer to prevent corrosion in the reactor. In this work, we studied the effect of different surface cleaning treatments on the boehmite scale formation on Al 6061 using time-of-flight secondary ion mass spectrometry (ToF-SIMS) and x-ray photoelectron spectroscopy (XPS). ToF-SIMS provides label free and matrix free surface analysis and imaging. A complementary technique is XPS due to its surface sensitivity and ability to determine chemical and oxidation states present. In this talk, we present spectral and imaging analysis of the nanometer scale boehmite layer formed on aluminum alloy surfaces as a function of surface cleaning technique. ToF-SIMS spectral analysis shows boehmite formation on all the samples and these results are corroborated with those of XPS. ToF-SIMS spectral principal component analysis (PCA) shows a trend of surface oxidation under different pH. The boehmite interface was also analyzed using high spatial resolution ToF-SIMS imaging and XPS depth profiling. The combined ToF-SIMS and XPS approach would enhance our understanding of the nucleation of boehmite phase on these varied aluminum surfaces.

AS-Contributed On Demand-34 Using Polyamide Films Grown by Molecular Layer Deposition (MLD) on Si(111) to Form 3C-SiC Thin Film*, Rustam Amashaev,* Dagestan State University, Russian Federation*; I. Abdulagatov,* Dagestan State Uiversity, Russian Federation

Silicon carbide (SiC) is a well-known technologically important material that has many industrial applications. Thin films of SiC can be deposited by chemical vapor deposition (CVD), physical vapor deposition (PVD), or atomic layer deposition (ALD) methods, however, these techniques cannot fulfill all the industrial needs in terms of thickness control, conformality, and cost effectiveness. In this work, we explored an alternative two-step method to obtain SiC films on Si (Fig.1 in Supplemental) [1]. In the first step, MLD polyamide film deposited on silicon substrate. In the second step, the polyamide film on Si annealed at high temperatures and vacuum. Under vacuum, the hydrogen is removed from the organic film and the remaining carbon becomes a precursor in solid-state reaction with Si substrate. In contrast to other gas phase deposition techniques, MLD allows to deposit organic thin films thermally (without using plasma) with an atomic level precision and conformality. These special features of MLD enable to synthesize highly conformal and uniform SiC films. In order to demonstrate that, MLD polyamide film was deposited on Si(111) using trimesoyl chloride (TMC) and 1,2-ethylenediamine (EDA) chemistry at 120 ^{o}C [2]. Polyamide film growth rate on Si(111) was ~18.5 Å/cycle. Vacuum annealing of 1125 Å thick polyamide film for one hour at 1300 ^{o}C and 10^{-7} Torr pressure resulted in formation of ~221 Å thick crystalline film (Fig. 2a) in Supplemental). X-ray diffraction (XRD), Raman spectroscopy, and x-ray photoelectron spectroscopy (XPS) employed to analyze annealed samples, also confirmed the formation of single crystal 3C-SiC (b-SiC) film on Si(111). Suspended ~200 Å thick 3C-SiC membrane can be formed by Si sublimation (Fig.2b) in Supplemental). Thin SiC film membranes and cantilever beams can be used in applications, such as pressure sensors, electromechanical resonators, accelerometers, and gyroscopes [3]. In general, above described approach can be applied for controlled synthesis of other metal carbide thin films as well.

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AS-Contributed On Demand-37 GaAs/Si Surface Energy Engineering, Modeling, and Nano-Bonding™ for Solar Cells at Low Temperatures ≤ 220°C, *A. Gurijala, P. Penmatcha, S. Jandhyala, M. Sahal, W. Peng, T. Balasooriya, T. Diaz, M. Bertram, C. Cornejo,* Arizona State University; *K. Kavanaugh,* Simon Fraser University; *R. Culbertson,* ***Nicole Herbots***, Arizona State University

GaAs/Si tandem solar cells absorb wavelengths between 0.4 and 2 µm, and can theoretically achieve photo-voltaic conversion efficiency (PVCE) of 44%. However, current methods integrating GaAs to Si, such as hetero-epitaxy and Direct Wafer Bonding require T>400°C, leading to defects from thermal expansion mismatch in addition to lattice mismatch, and decrease PVCE. Residual native oxides also decrease PVCE.

Nano-Bonding^{TM} (NB) is a direct wafer bonding method using Surface Energy Engineering (SEE) instead of T>400°C to create more efficient solar cells. NB includes three steps at T≤ 220°C: SEE, nano-contacting, and bonding activation. SEE modifies hydro-affinity, measured via water contact angle Θ_{H2O} and surface energies, measured via g, by using wet chemical etching. SEE planarizes surfaces, terminates them via hydroxylated monolayers, and optimizes surface termination to yield 2-D Precursor Phases (2D-PP). 2DPP are metastable and planar at the nano- and micro-scales.

3 Liquid Contact Angle Analysis (3LCAA) measures Θ_{H2O} and γ, Ion Beam Analysis (IBA) measures absolute oxygen coverage, and X-Ray Photoelectron Spectroscopy (XPS) measures surface oxidation states. 3LCAA uses statistical analysis of contact angles from 3 liquids, water, glycerin, and 1-bromo-naphthalene across wafer diameters and the van Oss-Chaudhury-Good theory. High resolution IBA combines Nuclear Resonance with <111> channeling. XPS measures Ga and As oxidation states within 5 nm of the surface.

3LCAA detects reversal in hydro-affinity of GaAs and Si after SEE. Initially hydrophobic n^+GaAs(100) becomes hydrophilic after SEE. γ_{GaAs} increases by almost 50% from 33.4±1 mJ/m^2 to 60±2 mJ/m^2 after SEE. Initially hydrophilic p^+Si(100) becomes hydrophobic with a decrease in γ_{Si} by 24% from 60±2 mJ/m^2 to 48±3 mJ/m^2. IBA detects a decrease in oxygen on GaAs of 50% from 7.2±0.5 ML to 3.6±0.2 ML after SEE. XPS reveals that two times more Ga (40%) than As (20%) is oxidized. After SEE, As_2O_5 decreases by 13.5%, while As_2O_3 increases by the same amount. IBA and XPS correlate with 3LCAA. A 50% decrease in oxygen and increase in low oxidation states lead to higher density of dangling bonds, thus higher γ and hydrophilic surface.

After NB, Surface Acoustic Wave Microscopy reveals that 98±1% of GaAs successfully nano-bonds to Si at T≤220°C with compression and 48±1% bonds without compression. A model of the GaAs surface before and after SEE is proposed to explain the reactivity and low temperature Nano Bonding of GaAs to Si.

AS-Contributed On Demand-40 Surface Characterisation of sp^2 Carbon Materials – From Graphene to Nuclear Graphite, ***Sarah Coultas***, *J. Counsell, N. Gerrard,* Kratos Analytical Limited, UK; *C. Moffitt,* Kratos Analytical Inc; *C. Blomfield,* Kratos Analytical Limited, UK

Carbon, considered to have ~500 allotropes varying from zero- (0D) to three-dimensional (3D) structures, is the fundamental building block of biological macromolecules. In this role it exists primarily in the sp^3 form. In more recent decades material discovery has concentrated on sp^2structures - C_{60}, carbon nanotubes (CNTs), fullerenes, graphene, graphite. Here we will explore surface characterisation techniques analysing, characterising and understanding these new material classes.

We will examine several different graphite grades using X-ray photoelectron spectroscopy (XPS) and ultra-violet photoelectron spectroscopy (UPS) to characterise the surface and sub-surface, particularly with regards to the sp^2 and sp^3 carbon bonding content. A peak-fitting methodology will be illustrated. Etching modes for cleaning and depth-profiling will be shown using both monatomic Ar^+ ions and cluster Ar_n^+ ions - the former causing unwanted damage to the graphite structure with a dramatic increase in sp^3 content. Ion implantation will be discussed for medium and high energy ions which leads to a broadening of the C 1s line. The experimental protocols will also be extended to graphene, the 2D analogue of graphite.

AS-Contributed On Demand-43 Understanding the Intrinsic Stability of Solvated Electroactive Ions at Heterogenous Mg Interfaces, ***Venkateshkumar Prabhakaran***, *G. Johnson,* Pacific Northwest National Laboratory; *G. Agarwal, J. Howard, L. Curtis,* Argonne National Laboratory, USA; *L. Soule, S. Wi, K. Hankins, S. Thevuthasan, V. Shutthanandan, Y. Shao, R. Assary, K. Mueller, V. Murugesan,* Pacific Northwest National Laboratory

Chemical transformations of electrolyte constituents, such as solvent and solvated electroactive ions, at the Mg-metal electrode determine the evolution of the solid-electrolyte interphase (SEI) and define the performance of Mg batteries. The ability to determine the fundamental chemistry occurring at electrode-electrolyte interfaces (EEIs) during charge transfer processes as a function of both electric field strength and concentration gradient is necessary to enable the rational design of more efficient and robust electrochemical technologies for energy storage. The scientific challenge is to delineate convoluted interfacial interactions (*i.e.,* adsorption, coordination, reactivity and transport) and control reaction pathways that lead to formation of desired products over unwanted byproducts that can result in decreasing battery performance. Soft landing of mass-selected ions, a versatile approach to surface modification, is ideally suited to preparation of well-defined interfaces with predetermined electrochemically active ions. Herein, we achieved a substantial advancement in the understanding of such complex interfacial reactions on Mg battery electrodes employing precisely-defined layer-by-layer assembly of electrochemically active cations and solvated counter-ions with precisely-selected stoichiometry and concentration. As an example, ion soft landing combined with *operando* infrared reflection-absorption spectroscopy (IRRAS), Raman spectroscopy, and *in-situ* x-ray photoelectron spectroscopy (XPS) was used to characterize the decomposition of electrolyte anions and solvent molecules on Mg electrodes. Our *in-situ* multimodal analysis enabled the capture of spectroscopic signatures from key chemical transformations of electrolyte anions and solvent molecules on reactive metal surfaces. These experimental results were correlated with the evolution of the SEI layer predicted by theory to provide molecular-level insight into the reaction mechanisms. In summary, our joint experimental and theoretical approach allowed us to acquire a more delineated understanding of electrochemical transformations occurring across length scales in operating EEIs and will aid the rational design of improved and sustainable electrochemical energy technologies.

AS-Contributed On Demand-46 A New SIMS Method to Characterize Hydrogen in Polysilicon Films, ***Xuefeng Lin***, *A. Fucsko, K. Noehring, J. Brown, E. Gabriel, A. Regner, S. York, D. Palsulich,* Corporate Laboratory, Technology Department, Micron Technology. Inc.

Abstract: A new analysis protocol for profiling the hydrogen (H) concentration depth distributions in polysilicon (poly Si) thin films on Si oxide was developed by using secondary ion mass spectrometry (SIMS). Traditional SIMS determination of H concentrations in poly Si films is to monitor and collect the atomic H^-, but this analysis method presents some challenges for providing stable and repeatable H depth profiles, especially for shallow profiling in thinner poly Si films on thicker Si oxide films. In this paper, we present a thorough study of the SIMS characterization of H levels in poly Si thin films on Si oxide. We describe an approach for the use of cluster SiH^- instead of atomic H^- to determine the H concentrations. The utilization of the SiH^- cluster ion minimizes both H adsorption effects on the film surface regions and also sample surface charging effects arising from the Si oxide layer underneath, thus enhancing the secondary ion signal stability in poly Si films, as discussed with secondary ion energy distribution on the samples. This method differs from conventional SIMS analysis of H in thin films and significantly improves the data quality and accuracy. We can accurately characterize H levels in 100Å-7000Å poly Si films on 1000Å-5000Å Si oxide layers. This analysis approach also shows efficiency with significant time saving to avoid often needed multiple repeat analysis in monitoring H^- atomic ion due to both H adsorption effects on the film surface regions and the e-beam induced the charge compensation effects. This analysis approach may also reduce the sample surface contamination effects in H analysis and can be applied to analyze other similar materials, such as H in Si films on other insulator films. Fourier transform infrared spectroscopy (FTIR) analysis was used to study the Si-H chemical bonding information for investigating the nature of the SIMS collected SiH^- cluster ions. Both the H implant sample with no significant Si-H bonding, and the poly Si samples with high levels of H and the weak Si-H bonding, exhibited strong SiH^- secondary cluster ion intensities in our studies. This indicates thecluster ion signals arise from either the combination of Si and H ions through the physics formation process or weak chemically bonded Si and H.

*Index Terms:*Hydrogen, FTIR, Ion Energy, Polysilicon, SIMS

AS-Contributed On Demand-49 Crystal Anisotropy in Surface Energy Engineering(See) OF $LiTaO_3$(110) Piezo-Electric for Low Temperature (< 453 K) Nano-Bonding^{TM} to SI and A-Quartz SiO_2*, S. Prakash, M. Sahal, A. Elison,* ***Shreyash Prakash****, B. Baker, S. Narayan, L. Puglisi, R. Culbertson, N. Herbots,* Arizona State University

Voice activated chips require integration of piezoelectrics on Si to respond to sound. One group of piezoelectrics, Lithium-based metallic oxides ($LiXO_3$), are strong candidates for voice activated chips due to their large piezoelectric coefficient (d_{33}). $LiTaO_3$ has a d_{33} of 5.7 pC/N and $LiNbO_3$ has a d_{33} of 6.0 pC/N, whereas SiO_2 has a d_{33} of only 0.14-0.26 pC/N. This work investigates bonding piezoelectric $LiTaO_3$ to Si.

Monolithic integration of dissimilar materials combines each material into a continuous heterostructure. Current wafer integration methods include heteroepitaxy, which is ordered crystal growth on another crystal surface, and Direct Wafer Bonding (DWB), which bonds crystal wafers via high-temperature annealing. But $LiTaO_3$ has a highly anisotropic trigonal crystal structure, while Si, with its cubic diamond structure, is much more isotropic. Si cubic lattice spacing happens to be much smaller than $LiTaO_3$'s. This means that $LiTaO_3$ crystals are heavily mismatched to Si crystals in all three directions, by as much as 40% in the c-direction and 66% in the a-direction.

Hence, trying to bond $LiTaO_3$ to Si via heteroepitaxy would lead to very large mechanical strains and significant crystal defects at the bonding interface. In addition, the large lattice mismatch could also generate fractures in brittle $LiTaO_3$. Both heteroepitaxy and DWB also use temperatures above 400°C for wafer annealing. $LiTaO_3$ and Si have a very large coefficient of thermal expansion (CTE) mismatch: $LiTaO_3$ has a CTE of 18.3 x 10-6/K, which is roughly 8 times greater than Si's CTE of 2.3 x 10^{-6}/K, and about 25 times greater SiO_2's CTE of 0.75 x 10^{-6}/K. Moreover, $LiTaO_3$ decomposes into Ta_2O_5 and Li^+ at T > 400°C. Hence, neither heteroepitaxy nor DWB are suitable integration methods for bonding $LiTaO_3$ to Si. Therefore, this investigates Nano-Bonding^{TM,1} (NB) of $LiTaO_3$ to Si at room temperature.

NB uses Surface Energy Engineering (SEE) to modify the surface energies(γ^T) of crystal wafers into far-from-equilibrium states. SEE creates complementary, far-from-equilibrium two-dimensional precursor phases to catalyze bonding. SEE uses Three Liquid Contact Angle Analysis (3LCAA) and the van Oss-Chaudhury-Good theory to characterize and measure hydro-affinity (HA) and γ^T, which indicate the degree of interaction between the two surfaces. 3LCAA can map γ^T along different crystal orientations. Water contact angles on anisotropic $LiTaO_3$ are found to vary significantly by 40%, averaging 45 ± 5.4°, with a range of 17 ± 1°, larger than $3\sigma = 3 \times 5.4° = 16.2°$. The observed effect of anisotropy upon surface HA is then correlated with γ^T, which fluctuates ± 6% with crystal directions. The effect of crystal anisotropy on the NB of $LiTaO_3$ to Si will be discussed based on HA and γ^T variation.

AS-Contributed On Demand-52 Coincident XPS and Raman Analysis of Drug Composition Phases in a Pain-Killing Tablet*,* ***Paul Mack,*** Thermo Fisher Scientific, UK

The benefits of configuring a single surface analysis tool with both XPS and Raman spectroscopy has previously been demonstrated for materials such as TiO_2, MoS_2 and graphene.This multi-technique analytical method is particularly useful in the context of ion sputtering, such as using argon clusters to clean the PMMA residue from a graphene surface, where XPS can be used to monitor chemical/compositional changes and Raman can be used to detect whether the ion sputtering is damaging the graphene lattice.Another important use for the combined XPS/Raman approach is where the sample is optically homogeneous or sample features are optically invisible.Either XPS or Raman could be used to find the features/areas of interest, but once found, if the analyst has to move the sample to a completely separate tool for further analysis, then it will be very difficult to locate exactly the same analysis feature/area.

Coincident XPS/Raman, with both techniques set-up to look at the same spot on the same sample, is the ideal technique to analyse optically invisible or homogeneous samples.In this work, a pain-killing tablet was analysed to detect to the various drug components, using Raman to specifically identify the drug and XPS to quantify the elemental/chemical states and evaluate the functional groups in the organic compounds.XPS was also used to image the surface, with full C1s, N1s and O1s spectra collected at each imaging pixel.It was then possible to use processing techniques, such as Principal Components Analysis (PCA) or Non-Linear Least Squares Fitting (NLLSF) to generate chemically resolved maps of the tablet.

AS-Contributed On Demand-55 Advancing Multimodal Imaging of the Evolving Interface of Irradiated Materials*,* ***Xiao-Ying Yu****, J. Yao, S. Spurgeon, B. Matthews, S. Riechers, Z. Zhu, W. Luscher,* Pacific Northwest National Laboratory

Multimodal imaging has seen renewed interest in microanalysis and microscopy. Light microscopy and electron microscopy are the two main pillars in correlative imaging in microanalysis. More advanced chemical imaging tools, especially time-of-flight secondary ion mass spectrometry (ToF-SIMS) as a powerful imaging mass spectrometry technique, has got introduced into the repertoire of imaging and spectroscopy modalities in recent years. Sample preparation is an important aspect in enabling multimodal imaging of the same sample. The sequence of sample analysis is another crucial factor to consider in achieving successful results. In this talk, I will present recent multimodal imaging results of irradiated cladding samples from a commercial heavy water reactor to probe the evolving material interfaces. Because the cladding materials have been exposed to neutron irradiation, sample handling is demanding. We used SEM-FIB to lift out a small section of the sample from the cladding material to permit atomic force microscopy (AFM), ToF-SIMS, and transmission electron microscopy (TEM) multimodal imaging of irradiated cladding. When comparing irradiated vs. un-irradiated samples, 3D distributions of isotopic hydrogen and lithium of the cladding indicate unexpected material transport as a result of neutron irradiation. This novel analysis sequence of irradiated commercial water reactor cladding material demonstrates that the advancement of correlative imaging can bring more scientific understanding of the water reactor technology and improve technical applications in the future.

AS-Contributed On Demand-58 Quantum Considerations About the Magic Angle in XPS Equipment*,* ***Alberto Herrera-Gomez,*** Cinvestav-Unidad Queretaro, Mexico

Bragg diffraction is employed as a means for monochromatizing X-rays in various spectroscopies such as X-ray photoelectron spectroscopy (XPS), X-ray absorption, X-ray diffraction, etc. The Bragg reflection causes a partial polarization of the beam impinging the sample. In fact, Bragg-reflection is commonly employed as a means for polarizing X-ray beams [1]. It was not until year 2010 that the partial polarization caused by the monochromator in XPS instruments was reported as a required correction for the calculations of the electron core-level photoelectric cross section [2]; the associated correction could be up to 10%.

The partial polarization also affects the so-called "magic angle", which refers to the angle at which the photoelectric cross section does not depends on the core-level asymmetry factor. The quantification of the change on the magic angle is reported in Ref. [3]. The correction on the photoelectric cross-section was done by averaging over initial polarizations [2]. This is the rule employed when calculating cross-sections in optical and electron physics [4–6]. An issue that is not discussed in the textbooks is that this assumption implies that Bragg-reflected photons imping the sample as either σ-polarized or π-polarized with probabilities depending on the polarization direction of the photon before reflection (this is referred as the hypothesis of the collapse of the X-ray photon wave-function upon Bragg diffraction) [3]. The other possibility is that the reflected photons are elliptically polarized. This is assumed in important works such as that described by Hart in 1978 [7]. In the first case, the magic angle (58.7°) differs by 4° from the value usually employed (54.7°). In the second case, the magic angle only changes by 2°. The experiments required to distinguish between the two cases will be discussed.

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AS-Contributed On Demand-61 Optimization and Characterization of Isotopically-Labeled, Epitaxial Fe_2O_3 and Cr_2O_3 for Diffusion Studies*, **Tiffany Kaspar**, S. Taylor, K. Yano,* Pacific Northwest National Laboratory*; T. Lach,* Oak Ridge National Laboratory*; Y. Zhou,* Pacific Northwest National Laboratory, USA*; Z. Zhu,* Pacific Northwest National Laboratory*; A. Kohnert,* Los Alamos National Laboratory*; E. Still, P. Hosemann,* University of California at Berkeley*; D. Schreiber,* Pacific Northwest National Laboratory

In virtually every area of materials science, it is critical to understand the movement of atoms within solids under external stimuli such as temperature, pressure, electric fields, magnetic fields, irradiation, chemical gradients, and/or concentration gradients. This movement often takes the form of diffusion. In oxides, anion and cation diffusion can be significantly different, and both can be dependent on factors such as oxide stoichiometry and/or oxygen activity in equilibrium with the oxide, which greatly increases the complexity of observed phenomena. This diffusion is exploited for energy generation and storage in, for example, batteries and solid oxide fuel cells, and electronic devices such as resistive switching memory. Irradiation by energetic particles alters both the magnitude and the mechanism(s) of diffusion in solids by introducing a non-equilibrium population of vacancies and self-atom interstitials as a result of atomic displacements. This high concentration of defects serves to enhance diffusion, significantly impacting microstructural evolution in radiation environments. Here, we present a universal approach to the deposition of epitaxial oxide thin films in which anions, cations, or both can be isotopically enriched at specific locations within the film stack. We demonstrate this approach using epitaxial thin films of Fe_2O_3 and Cr_2O_3 in which precisely-defined layers isotopically enriched in ^{18}O and/or ^{57}Fe have been included. Complementary characterization by scanning transmission electron microscopy (STEM), atomic probe tomography (APT), and secondary ion mass spectrometry (SIMS) establishes the position, concentration, and interfacial abruptness of the isotopically-enriched layers. We demonstrate the utility of this approach by quantifying oxygen and cation self-diffusion in pristine epitaxial Fe_2O_3 and Cr_2O_3, as well as at structural defects in mixed-phase epitaxial Fe_2O_3/Fe_3O_4. Diffusion induced by thermal annealing is compared to that enhanced by proton irradiation by quantifying the distribution of an ^{18}O (and in some cases, ^{57}Fe) layer intentionally placed within the oxide thin film.

AS-Contributed On Demand-64 Adsorption Study of L-Cysteine Self-Assembled Monolayers on Au (100) Surface by Scanning Tunnelling Microscopy and Ab-Initio Methods*, V. Franco, S. Rodríguez-Sotelo ,* Instituto de Física del Litoral (CONICET-UNL), Argentina*; G. Ruano-Sandoval,* Centro Atómico Bariloche (CNEA), Argentina*; M. Passeggi (h),* Instituto de Física del Litoral (CONICET-UNL) , Argentina*; **Florencia Calaza**,* Instituto de Desarrollo Tecnológico para la Industria Química (CONICET-UNL), Argentina

The functionalization of metal surfaces by biological molecules has a growing number of applications in various fields. For this, it is essential to understand the chemical and physical properties of the organic /inorganic interface and the formation process of self-assembled monolayers (SAM's) of biological molecules such as amino acids. L-cysteine (Cys) is a particularly interesting amino acid as a macromolecule binder and chemical sensor. In this work, we carry out a theoretical and experimental study of the formation of SAM's of Cys molecules on monocrystalline surfaces of Au (100), in order to clarify the molecular adsorption mechanism. The adsorption of molecules was performed by dipping the substrate in methanolic solutions of Cys at different coatings and characterized by scanning tunneling microscopy (STM) in air and at room temperature. Additionally, the substrate-adsorbate interaction was studied with ab-initio calculations using the Density Functional Theory (DFT) in three systems: (i) Cys on Au (100), (ii) Cys trimers on Au (100) and (iii) Methanol on Au (100), to determine the equilibrium configurations, adsorption energies and distances, state densities and charge transfer between the substrate and the molecule.

By scanning tunnel microscopy, the molecular structure, order and reconstruction that induce the chemisorption and /or physisorption process of these molecules in the substrate were examined. It is revealed a pattern in the form of rectangular bands of Cys molecules, adsorbed as multilayers on Au (100). The calculations showed that the physisorption processes of Cys on Au (100) are mainly directed by the interaction between the thiol group and gold. The most stable configuration and the difference in charge density induced by the interaction, for this system, indicate that the amino acid is in its zwitterionic form. Furthermore, it was determined that the amino functional group moves away from the gold surface with a positive charge density, exposing the carboxyl group with a negative charge density closer to the surface; which would explain the chemical composition of SAM's. The latter possibility was tested by ATR-IR (Attenuated Total Reflectance-IR) to try identifying which groups of the molecule are interacting more strongly with the surface Au atoms.

AS-Contributed On Demand-67 Navigating Disorder in Superconductors Using Atomic-Scale Imaging and Machine Learning*, **Petro Maksymovych**,* Oak Ridge National Laboratory

Disorder is a powerful approach to elicit and control superconducting properties, as evidenced from record Tc's, quantum phase transitions and exotic quasiparticles, predicted or evidenced from disorder interacting with the superconducting order parameter. Capturing and understanding effects of disorder necessitates bridging length, energy and temporal scales - a persistent challenge for experiment and theory. Here we will categorize disorder in notoriously heterogeneous atomic-scale images of unconventional superconductors. From the information centric point of view, understanding the structure of these datasets amounts to effective and physically meaningful data compression. We will discuss compressibility of various kinds of STM data setting up the context for techniques of compressive sensing, machine learning and information theory as a way to understand the results of the experiments and improve data acquisition. We will promote similarity learning as a consistent strategy to categorize disorder with minimum prior knowledge. And finally, we will show how disorder helps understanding the STM technique itself, using statistical identification of Josephson currents in tunneling microscopy. Research sponsored by Materials Science and Engineering Division, US DOE and Center for Nanophase Materials Sciences, Oak Ridge National Lab, a DOE Office of Science user facility.

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AS-Contributed On Demand-70 Overview of *JVST A* Collection of Guides and Best Practices for XPS*, **Don Baer**,* Pacific Northwest National Laboratory*; K. Artyushkova,* Physical Electronics USA*; C. Easton,* CSIRO Manufacturing, Australia*; M. Engelhard,* Pacific Northwest National Laboratory*; G. McGuire,* Adámas Nanotechnologies, Inc.,*; A. Shard,* National Physical Laboratory, U.K.

The rapid growth in the use of XPS around the world has introduced the technique to a wide range of researchers in many disciplines with important areas of application. Unfortunately, the experience and practices well established in the XPS community have not as readily transferred to this growing group of new users. This has led to a significant number of inaccurate, misleading or fundamentally incorrect applications of XPS or analysis of XPS data as reported in the literature. In response to the issue, and the more general reproducibility challenges, the Journal of Vacuum Science and Technology A has published a collection of papers under the heading *Reproducibility Challenges and Solutions with a focus on XPS.* Because of the wide use of XPS, a series of XPS guides and protocols were included in this collection. This talk provides an overview of the information provided by the papers. The approach taken to assembling the guides was to break the overall topic into guides that address specific areas or issues. Some papers are relevant to most types of XPS studies while others focus on applications of XPS to specific areas or topics. General XPS topics covered in one or more papers include an introduction to XPS and issues related to quantification, backgrounds in XPS spectra, peak fitting, electron path lengths important to analysis, dealing with insulators and surface charging, the importance of consistent terminology, instrumentation performance checks, information about relevant international standards, and data conversion and storage. These guides are intended to be more introductory than comprehensive although they point readers towards relevant literature that covers some topics in greater depth. The application area guides are intended to provide specific information related to the use of XPS in important areas. These guides address XPS analysis of polymers, catalysts, semiconductors and nanoparticles. This collection of papers has been developed in response to a survey and discussions that identified needs for tools that can help the community address reproducibility issues. In addition to presenting a summary of this collection, we request feedback from the community and suggestions for other tools that can assist the AVS in addressing consistency and reproducibility challenges, especially in areas of importance to surface analysis. A list of papers in the collection can be found at:

https://avs.scitation.org/toc/jva/collection/10.1116/jva.2020.REPROD2020.issue-1.

AS-Contributed On Demand-73 Surface Functionalization and Atomic Layer Deposition of Binary Metal Oxides on MoS_2 Surfaces*, Theodosia Gougousi*, *J. Kropp, C. Ataca,* UMBC

Transition metal dichalcogenides (TMD) have been studied for device applications due to their electronic properties and their possession of a bandgap (1.8eV for single layer MoS_2).The fabrication of electronic devices requires deposition of high-quality dielectrics on the hydrophobic TMD surface and remains a challenge.

In this work we will provide examples of TiO_2 and Al_2O_3 Atomic Layer Deposition (ALD) film growth from tetrakis dimethyl amino titanium (TMDAT), trimethyl aluminum (TMA) and H_2O at 100-200°C on exfoliated and Chemical Vapor Deposition (CVD) MoS_2 flakes. We find that the initial surface condition of exfoliated MoS_2 flakes varies greatly due to residual adhesive contamination resulting in large variation in the film morphology. More controlled growth is obtained for CVD MoS_2 flakes but even in this case the surface coverage is thickness dependent for films as thick as 10 nm.

In order to alter the surface energy, seeding with inorganic and organic species have been investigated. Mercaptoethanol (ME) is a small thiol that contains a -SH functional group at one end and -OH termination at the other end. The -SH termination is expected to react with the MoS_2 surface leaving the surface -OH terminated as desired for the onset of the ALD chemistry. Atomic Force Microscopy (AFM) measurements confirm that ME treatment alone does not promote more uniform film growth. Computational studies of the ME-MoS_2 surface interaction using Density Functional Theory (DFT) reveal that ME interacts with the sulfur vacancies almost exclusively. Vacancy density is less than ~5% for as-deposited CVD MoS_2, and depositions result in non-continuous coverage for typical thermal ALD.Argon ion sputtering was used to remove Sulfur atoms from the surface and increase the vacancy density up to ~20%. AFM confirms the formation of continuous 6 nm TiO_2 films at 100°C for both ME treated and control samples.DFT calculations reveal that TDMAT can interact directly with the vacancy. However, the calculated Density of States for these defect rich surfaces contain gap states that are undesirable for high quality devices. Treatment of defect rich surfaces with ME results in the removal of the gap states which is expected to result in good electrical properties.

$HAuCl_4$ solutions have been also used to seed the surface with -Cl terminal species to initiate film growth. XPS data confirm both the presence of Au on the surface and absence of residual chlorine. AFM shows only partial surface coverage for films as thick as 6 nm. A distinct difference in the film morphology is obtained though as a result of this treatment indicating that the film growth mechanism has been altered.

AS-Contributed On Demand-76 Elucidating the Lubrication Mechanism of Ionic Liquid: a Multi-technique, Nanoscale Spectroscopy and Microscopy Study*, Filippo Mangolini*, *Z. Li, O. Morales-Collazo,* The University of Texas at Austin*; J. Sadowski,* Brookhaven National Laboratory*; H. Celio, A. Dolocan, J. Brennecke,* The University of Texas at Austin

Ionic liquids (ILs) have recently gained considerable attention owing to their unique and tunable physico-chemical properties (*e.g.*, low vapor pressure, high thermal stability), which have made them useful for a range of applications, including energy storage, catalysis, and lubrication. ILs are particularly attractive in lubrication, since their properties make them suitable for components working under extreme conditions, such as those found in engines and spacecraft. When ILs are used as lubricants, the interface between the IL and the sliding surfaces plays a pivotal role in controlling the friction and wear response. Despite the weight of published literature, remarkably little is still known about the lubrication mechanism of ILs. The development of a fundamental understanding of the mechanism by which ILs reduce friction and/or wear requires shedding light on the processes occurring at nanoscale asperities within macroscale contacts. This constitute a significant challenge that requires the use of complementary surface-analytical techniques to understand the nanoscale mechanisms at play.

Here, we used atomic force microscopy (AFM) to visualize and quantify the processes occurring at sliding interfaces *in situ*, in single-asperity nanocontacts. The AFM tests, in which a diamond tip was slid on iron in phosphonium phosphate IL (PP-IL), indicated a significant friction reduction only after the removal of the native surface oxide from iron. Even though the AFM experiments allowed for the identification of changes in topography and friction, they could not provide any information about the composition of the regions scanned by AFM. The analysis of these regions is a challenging surface science problem owing to their limited dimensions and the small thickness of the surface material modified by the mechanical action of AFM tips. To address this challenge and elucidate the origin of the friction reduction observed by AFM, a multi-technique approach was employed. The results of laterally-resolved *ex situ* analyses of the surface chemistry of steel by synchrotron-based X-ray photoemission electron microscopy, low energy electron microscopy, and time-of-flight secondary ion mass spectrometry indicated that the mechanically-induced exposure of metallic iron during AFM tests carried out in PP-IL leads to an increase in surface coverage of adsorbed phosphate anions together with a change in surface potential. Based on these results and atomistic simulations of the configuration geometry of phosphate ions on metallic and oxidized iron, a simple phenomenological model is proposed to account for the observed lubrication behavior.

AS-Contributed On Demand-79 Hydrogen Detection by SnO_2-Based Core-Shell Nanowires With Varying Shell Thicknesses Grown by Atomic Layer Deposition*, Muhammad Hamid Raza,* Humboldt-Universität zu Berlin, Germany*; N. Kaur, E. Comini,* University of Brescia, Italy*; N. Pinna,* Humboldt-Universität zu Berlin, Germany

Hydrogen is one of the most potent energy vectors due to its low weight, high catalytic values, non-pollution, and high abundance. There is a need for quick and sensitive hydrogen detection, due to its nature as a colorless and odorless extremely flammable gas with a low explosive limit (4%, 40000 ppm) in air. SnO_2 nanostructures have been extensively reported semiconducting metal oxide (SMOX) for gas sensing. The sensitivity and selectivity of these nanostructured can be enhanced by employing them with the secondary materials.However, control over the thickness of the shell layer is essential; in particular, a thin shell layer may influence the charge conduction channel by modulating the space charge layer near the interface. Here, two different SnO_2-based core-shell nanowires (CSNWs) are synthesized with the loading of *p*-type SMOX (NiO) and insulating (SiO_2) films as secondary materials onto the SnO_2 nanowires. Atomic layer deposition (ALD) was used to deposit varying thicknesses of NiO and SiO_2 shell layers. Interestingly, both the heterostructures are found to exhibit enhanced sensitivity to hydrogen in spite of underlying different sensing mechanisms. Importantly, the thickness of the shell layer plays a significant role in both types of heterostructures., *i.e.*, SnO_2-NiO and SnO_2-SiO_2 CSNWs. A comparison of enhanced selectivity and sensitivity after the ALD grown shell-layers will be presented in terms of *p*–*n* heterojunction (SnO_2-NiO CSNWs) vs. molecular sieve action (SnO_2-SiO_2 CSNWs).

AS-Contributed On Demand-82 X-Ray Absorption Near Edge Structure (XANES) Measurements of Oxides Formed on High Entropy Alloys*, Anil Krishna Battu*, *B. Gwalani, T. Suntharampillai, A. Devaraj,* Pacific Northwest National Laboratory

High entropy alloys (HEA) exhibit an excellent combination of properties, providing motivation to novel alloy development with single or multiphase microstructures. High temperature application of HEAs requires comprehensive understanding of phases tability and environmental degradation. The equiatomic CrMnFeCoNi based alloy, also known as Cantor alloy, is a widely studied single-phase alloy for its superior structural properties. However, recent studies have demonstrated the formation of secondary phase during the annealing in the intermediate temperature ranges. We investigated the structural and chemical changes in Cantor alloy during elevated temperature oxidation using in situ and ex situ approaches along with the influence of Al addition to the alloy composition. We utilized Cr, Mn, Fe, Co and Ni L edge X-ray absorption near edge structure (XANES) measurements to understand the chemical changes in the material. The structural and phase changes were analyzed using transmission electron microscopy (TEM) and atom probe tomography (APT). The oxidation states of the elements can be clearly identified from the XANES spectra and correlated to the phase information obtained from TEM and APT. Addition of Al changes the oxide chemistry, material vulnerability to oxidation and these details will also be discussed.

AS-Contributed On Demand-85 Laser Desorption Postionization vs. Secondary Ion Mass Spectrometry for Imaging of Organic Biomarkers in Geological Sample*, R. Wickramasinghe, M. Pasterski,* University of Illinois at Chicago*; A. Ievlev, M. Lorenz,* Oak Ridge National Laboratory*; I. Veryovkin, F. Kenig,* ***Luke Hanley****,* University of Illinois at Chicago

Multidimensional gas chromatography mass spectrometry (MS) has been used to detect organic biomarkers within bulk extracts of geological samples [1]. However, it is difficult to rule out the possibility of organic contamination in such studies due to the loss of spatial information during sample preparation. MS imaging and other spatially resolved sampling methods can overcome these shortcomings by identifying organic biomarkers within intact geological samples and correlating such MS data with petrographic and fluorescence images. Secondary ion mass spectrometry (SIMS) imaging is currently the premier method for identifying organic biomarkers within geological samples [2], but suffers from extensive ion fragmentation that can limit molecular identification.

A novel MS imaging strategy is described here that seeks to improve upon SIMS imaging of organic biomarkers within geological samples. Femtosecond laser desorption postionization mass spectrometry (fs-LDPI-MS) employs 800 nm, ~75 fs laser pulses for ablation of neutral organic molecules from a thin prepared slice of a geological sample, followed by postionization using 157 nm (7.9 eV) laser pulses and subsequent detection by a time-of-flight mass analyzer [3].

The high lateral resolution of fs-LDPI-MS imaging and its ability to detect molecular species with lower fragmentation relative to SIMS allows for high resolution MS-imaging and identification of isolated sample features. Multimodal imaging of geological samples with high organic content is conducted with Bi ion ToF-SIMS, fs-LDPI-MS, petrographic, and fluorescence imaging. SIMS and fs-LDPI-MS specifically are compared for their relative ability to identify organic biomarkers confined to micron-sized regions within intact geological samples.

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AS-Contributed On Demand-88 Box Plots: A Simple Graphical Tool for Visualizing Overfitting in Peak Fitting as Demonstrated with X-ray Photoelectron Spectroscopy Data*,* ***Behnam Moeini****, H. Haack,* Brigham Young University*; N. Fairley,* Casa Software Ltd, UK*; V. Fernandez,* CNRS, Institut des Matériaux Jean Rouxel, IMN, Université de Nantes, France*; T. Gengenbach , C. Easton,* Commonwealth Scientific and Industrial Research Organization (CSIRO) Manufacturing, Australia*; M. R.Linford,* Brigham Young University

Peak fitting of spectra/data is frequently performed in science. However, recent reports suggest that the quality of this peak fitting in the scientific literature is often inadequate. An important step towards improving the peak fitting in the literature is to develop the expectation/culture that the testing of one's fitting protocol, along with the presentation of such tests, is necessary for confirming the validity of a fit. The development of new methodologies that enable researchers to visualize the qualities of their fits that are straightforward to implement will aid in this effort. In this paper we describe a new statistical tool for determining the quality of protocols for fitting data. This tool, box plots of the results of random starting conditions, helps identify multiple local minima in a multidimensional fit space of the fit parameters. Ideally, there should be a single global minimum for a fitting protocol such that different, reasonable starting conditions lead to the same result. To determine whether a fit space contains multiple local minima, a series of reasonable, random starting conditions are chosen for the fit. If the boxes in the box plot of the peak areas of these fits are narrow, the different possibilities converge to a single global minimum. Conversely, if the boxes are wide, multiple local minima are present. This method is similar to the mathematical concept of 'disproof by contradiction'. Our approach is demonstrated with four- and ten-component fits to a moderately complex C 1s X-ray photoelectron spectroscopy (XPS) narrow scan. The resulting box plots compare favorably to results of traditional Monte Carlo analyses and uniqueness plots, where box plots are applied to Monte Carlo results, although each of these statistical tools performs a different function/probes a fit space/protocol differently.

AS-Contributed On Demand-91 A New Compact Electron Detector for REELS and Elastic Peak Spectroscopy*,* ***Philippe Staib****,* Staib Instruments

Several analysis techniques are performed using a new single electron detector mounted into an SEM chamber. The primary applications are REELS and Elastic Peak Spectroscopy (EPS) at primary beam energies up to 5000 eV.The detector is an energy analyzer with multiple operating modes:

- Imaging the secondary electron SE and back scattered secondary electrons BSE signals with precise selection of the energy range.

- Imaging the Elastic peak and measurement of its intensity and energy position.

The measurement and mapping of the elastic peak fully separated from energy losses is a powerful technique for sample characterization. The peak intensity is determined by the elastic backscattering cross section and primarily depends on the atomic number Z thus sensitive to the atomic composition (identification of phases). Measurements also reveal minute changes of the crystal structure. The energy position is determined by the recoil energy loss, owing to the conservation of energy and impulse, and depends on the atomic mass M of the target atom. The energy of the elastic peak shows shifts expected from the recoil loss energy, measurable, in this case, for lower Z materials from H up to O.

- Measuring energy losses of characteristic energy losses (CEL) especially the low energy valence band region and band gap of semiconductors.

- Mapping the spatial distribution of energy losses.

- Mapping the photon emission (cathodo- luminescence, surface plasmon decay) by setting the analyzer above the primary energy in order to block the electron signal.

When operating at higher beam current intensities, Auger electron spectroscopy (AES) and measurement of the total X-ray yield are possible. Diffraction patterns are observed at higher primary beam energy when adjusted to a grazing incidence angle to the surface (EBSD or RHEED).

These operating modes are illustrated by results obtained on metals, semiconductors and biological samples, and also show the necessity of a clean, carbon free, vacuum environment to gain the most from these capabilities.

The various operating modes of the detector are selected simply by adjusting its control voltages of the and are easily computer controlled. The detector works up to 5,000 eV, a beam energy well suited to SEM columns. The electronically adjustable energy resolution can reach 1eV to provide accurate measurements of the elastic peak and energy losses. The sensitivity, resulting from the analyzer's large acceptance solid angle, allows work in the nano ampere beam current range for most applications. Combining these capabilities in a single energy detector adds new analytical tools to SEM.

AS-Contributed On Demand-94 In Situ Spectroscopy Beamline at the Swiss Light Source*,* ***Zbynek Novotny****,* University of of Zürich & Paul Scherrer Institute, Switzerland

A new In Situ Spectroscopy beamline (X07DB) has been recently established at the Swiss Light Source (SLS). The beamline is now open to the user community *via* proposal access, offering studies of solid-gas and solid-liquid interfaces using ambient-pressure X-ray photoelectron spectroscopy. Two experimental endstations are available, capable of studying "real" catalysts such as polycrystalline/powder samples under catalytically relevant conditions, as well as model systems represented by well-defined single crystals prepared under UHV conditions. The unique capability of the beamline is the ability to perform electrochemical studies. Besides our current experimental capabilities, I will present the ongoing in-house research, instrumental development, and plans towards the scheduled upgrade of the SLS 2.0.

AS-Contributed On Demand-97 The Frequency with which the Elements are Researched and their X-ray Photoelectron Spectroscopy (XPS) Narrow Scans are Shown in the Scientific Literature*, G. Major, G. Pinto, V. Carver,* Brigham Young University*; C. Easton, T. Gengenbach,* CSIRO Materials Science and Engineering, Australia*; W. Skinner,* Future Industries Institute, University of South Australia, Australia*; D. Baer,* Pacific Northwest National Laboratory*; T. Nunney,* Thermo Fisher Scientific, UK*;* ***Matthew Linford,*** Brigham Young University

A recent report written by some of us (Linford … Baer, Microscopy and Microanalysis 2020) indicates that more than 30% of the X-ray photoelectron spectroscopy (XPS) narrow scans in the scientific literature are incorrectly analyzed. In this context, we present a discussion of the frequencies with which the different elements are researched for XPS peak fitting and reported in the scientific literature. That is, we have correlated the number of page views from XPS Simplified, which is an often-accessed online database on XPS peak fitting, with the numbers of narrow scans for the different elements that are published in different materials journals. In general, there is good correlation between the elements on these lists (especially between the top ten elements on both lists, but less so among the next ten), with carbon and oxygen being the top two elements on both lists. In this analysis, it became clear that there are certain elements that are more researched on XPS Simplified and less shown in the literature, and vice versa. A possible interpretation for these results is that those elements that are more often shown in the literature and less researched are considered by the community to be more straightforward or easier to analyze, while those that are less shown and more researched are considered to be harder. We compare these perceptions of ‘easier’ and ‘harder’ to the accuracy with which these elements are analyzed in the literature. Also, in an effort to better understand the two most commonly researched and published-on elements (C and O) in XPS, we discuss the types of carbon- and oxygen-containing materials that are most often analyzed by XPS in the literature. That is, we will present the fraction of papers that show carbon analysis of polymers vs. graphitic carbon materials (graphene, carbon nanotubes, C60 fullerenes, etc.) vs. adventitious carbon, etc. For oxygen, we discuss the fraction of papers that show XPS analysis of inorganic oxides vs. polymers. Finally, using principal component analysis (PCA), we discuss the differences and similarities between the different journals and XPS Simplified vis-à-vis the different elements that are shown or researched.

AS-Contributed On Demand-100 Correlative Experimental and Theoretical Investigations of the Interfacial Bond Formation of Ti, Al, and TiAl Thin Films Deposited on Polycarbonate*,* ***Lena Patterer****, P. Ondracka, D. Bogdanovski, L. Jende, J. Schneider,* RWTH Aachen University, Germany

To systematically investigate the interfacial bond formation between poly(bisphenol A carbonate) (PC) and TiAl thin films, this study explores also the individual effects of Ti and Al on the bond formation at the interface. Therefore, thin metallic layers (Ti, Al and TiAl) were deposited onto PC substrates by direct current magnetron sputtering and the forming interface was subsequently analyzed by X-ray photoelectron spectroscopy (XPS). In addition to the experimental analysis, density functional theory molecular dynamics (DFT-MD) simulations of a thermalized PC dimer interacting with the corresponding metallic surfaces were carried out to study the interface regarding reactivity, bond density and bond strength. To this end, selected configurations at various simulation times were used to determine changes in the chemical state of the polymer in comparison to the experimentally detected changes. Consistent with DFT predictions, XPS data indicate a high reactivity of Ti towards PC. Reactions between Ti atoms and all functional groups of PC are observed, resulting in the formation of interfacial C-Ti as well as (C-O)-Ti bonds for Ti and TiAl thin films. In contrast, Al is less reactive and reacts only with the carbonate group to form (C-O)-Al bonds at the interface. However, integrated crystal orbital Hamilton population calculations indicate a significantly higher bond strength for interfacial (C-O)-Al bonds (up to −5.6 eV) compared to interfacial (C-O)-Ti and C-Ti bonds (both up to −2.6 eV).

In summary, the experimentally obtained density of interfacial bonds is significantly higher for the Ti thin film compared to the Al thin film, but the bond strength between Al atoms and the carbonate groups is higher. By multiplying the experimentally determined relative interfacial bond concentration with the theoretically determined bond strength as an indicator for adhesion, Ti exhibits a more than five-times higher value compared to the Al thin film. Consequently, this study is unequivocal evidence of Tithin films being the preferential choice as adhesion interlayers for PC.

AS-Contributed On Demand-103 Analysis of XPS Depth-Profile Data Using Maximum Likelihood Reconstruction: Extracting Sample Structure and Sputtering Parameters*,* ***Lev Gelb****, A. Walker,* University of Texas at Dallas

We present progress in the simutaneous quantitative extraction of both sample structure and composition and sputtering parameters from XPS depth-profiles of multilayer films. Such data are typically used to obtain the apparent fractional composition of each element as a function of depth. These results are apparent because the analysis assumes the elements are homogeneously distributed in the probed region, a condition which necessarily does not hold near interfaces. Furthermore, the sputtering process leads to roughening, in-sample mixing, and changes in sample composition, which also lead to further distortions.

Our approach to analysis of depth profiles is first to 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.

We first demonstrate the basic idea and explore the type of results that can be obtained using synthetic data. The resolution of the extracted depth profiles improves when additional peaks are incorporated in the analysis. This is especially true when peaks at very different energies are used, as they have very different inelastic mean free paths and so provide complementary information. We then reconstruct experimental data from several well-characterized samples and discuss the results obtained. Finally, the possibility of optimization against complete spectra (rather than extracted fractional compositions) and inclusion of angle-resolved data are considered.

AS-Contributed On Demand-106 Formation of Black Silicon-Like Nanostructures During Flat-Top Femtosecond Laser Ablation in Atmosphere*,* ***Jason Gross****, L. Hanley,* University of Illinois at Chicago

The fluence and transverse optical intensity profile of a laser beam are crucial parameters for high resolution depth profiling analysis of materials by femtosecond laser ablation (fs-LA) mass spectrometry. When a conventional Gaussian-shaped fs beam is used for ablation, material removed from the crater walls leads to artifacts in the depth profile. This same Gaussian fs beam can be conditioned into a flat-top shape with homogenized fluence and used for fs-LA in atmosphere. Ablation with the flat-top fs beam appears to prepare nearly cylindrical craters with flat valleys on silicon across a broad range of incident angles when viewed by optical 3D microscopy. However, scanning electron microscopy (SEM) shows that these supposed craters are instead actually filled with amorphous black silicon-like structures that protrude away from the silicon surface. Black silicon is the generic name for nanostructured silicon with very high optical absorption properties that prior work has shown can be formed by fs-LA and other methods. By contrast, Gaussian fs-LA in atmosphere yields craters as observed by both optical 3D microscopy and SEM. Near ablation threshold fluences have been shown to yield these black silicon structures. The absorption range, absorption efficiency and shape of black silicon are directly affected by the experimental parameters used to form it. As shown in the figure below, the structures obtained from ablating silicon with flat-top fs-LA are irregular structures that deviate from the typical conical and/or cylindrical, partially ordered black silicon nanostructures previously reported in the literature.

AS-Contributed On Demand-109 Laboratory Based Hard X-ray Photoelectron Spectroscopy*,* ***Marcus Lundwall,*** Scienta Omicron, Sweden*; B. Giles,* Scienta Omicron

Hard X-ray photoelectron spectroscopy (HAXPES) is generally used to study core topics in condensed matter physics. However, with a worldwide increase in the number of HAXPES focused endstations, many other interest groups now recognize its broad appeal.In a HAXPES experiment 2-10 keV X-rays are used to excite photoelectrons to study the chemical environment and electronic structure of materials non-destructively. In contrast to standard XPS, HAXPES is more sensitive to what is beneath the surface. This makes it an ideal technique for studying structured samples that cannot be analyzed using traditional XPS. Bulk sensitivity means that realistic samples can be investigated without the need for surface preparation. Unfortunately, there are very few existing HAXPES systems. Most are predominantly located at synchrotrons, as the photoionization cross sections at high energies is small and necessitates large X-ray intensities.This work shows a new laboratory based HAXPES instrument capable of delivering monochromated 9.25 keV X-rays in a focused 30x45

μm^2 X-ray spot with energy resolution <0.5 eV. Systematic reference measurements demonstrate the system's capability. Application based results from various fields, including in operando measurements on devices and studies of energy related materials, are also presented.

AS-Contributed On Demand-112 Unravelling the Ion-Energy-Dependent Structure Evolution and Its Implications for the Elastic Properties of (v,Al)NThin Films*, Soheil Karimi Aghda,* Chair of Materials Chemistry (MCh), RWTH Aachen University, Germany*; D. Music,* Department of Materials Science and Applied Mathematics, Malmö University, Sweden*; Y. Unutulmazsoy,* Leibniz Institute of Surface Engineering (IOM), Germany*; H. Sua, S. Mráz, M. Hans,* Chair of Materials Chemistry (MCh), RWTH Aachen University, Germany*; D. Primetzhofer,* Department of Physics and Astronomy, Uppsala University, Sweden*; A. Anders,* Leibniz Institute of Surface Engineering (IOM), Germany*; J. Schneider,* Chair of Materials Chemistry (MCh), RWTH Aachen University, Germany

Ion irradiation-induced changes in the structure and mechanical properties of metastable cubic (V,Al)N deposited by reactive high power pulsed magnetron sputtering are systematically investigated by correlating experiments and theory in the ion kinetic energy (E_k) range from 4 to 154 eV. Increasing (E_k) results in film densification and the evolution from a columnar (111) oriented structure at $E_k \leq$ 24 eV to a fine-grained structure with (200) preferred orientation for $E_k \geq$ 104 eV. Furthermore, the compressive intrinsic stress increases by 336 % to -4.8 GPa as $E_k$is increased from 4 to 104 eV. Higher ion kinetic energy causes stress relaxation to -2.7 GPa at 154 eV. These ion irradiation-induced changes in the thin film stress state are in good agreement with density functional theory simulations. Furthermore, the measured elastic moduli of (V,Al)N thin films exhibit no significant dependence on E_k. The apparent independence of the elastic modulus on $E_k$can be rationalized by considering the concurrent and balancing effects of bombardment-induced formation of Frenkel pairs (causing a decrease in elastic modulus) and evolution of compressive intrinsic stress (causing an increase in elastic modulus). Hence, the evolution of the film stresses and mechanical properties can be understood based on the complex interplay of ion irradiation-induced defecb generation and annihilation.

AS-Contributed On Demand-115 Monte Carlo Evaluation of Uncertainty in Hurst Exponents Computed from Power Spectral Analysis of Atomic Force Microscopy Images*, Robert Chrostowski,* *Z. Li, F. Mangolini,* University of Texas at Austin

At sufficiently fine scales, all surfaces exhibit texture, which influences adhesive, optical, thermal, and mechanical properties of materials. Accurately predicting surface finish-property relationships is challenging because common summary statistics for surface texture (such as root mean square slope or curvature) can differ by even orders of magnitude *for the same surface* depending on the scale that is probed. A scale-invariant description can be obtained from Power Spectral Density (PSD) analysis of atomic force microscopy (AFM) height maps by computing the Hurst exponent (which is related to the fractal dimension). While estimation of Hurst exponents from PSDs is a common analysis technique widely used in many disparate fields (from contact mechanics to astronomy), few studies exploring the *accuracy* of this estimation exist. Here, we use a Fourier filtering algorithm combined with a novel approach to simulate typical AFM scan-line anisotropy to generate synthetic AFM topography images with *known* input Hurst exponent. A Monte Carlo approach is then used to evaluate the uncertainty, including both variance and *bias,* in Hurst estimation from PSDs across different hypothetical experimental approaches. Our analysis reveals that estimates of the Hurst exponent from images collected at a single scale are persistently biased in a scale-dependent fashion despite misleading convergence in variance. This bias can be reduced by combining images collected at least at three different scales across the range of scales accessible to AFM.

AS-Contributed On Demand-118 Spatially Resolved Molecular Compositions and Formation Mechanisms of Insoluble Engine Deposits Uncovered Using 3D OrbiSIMS*, Max Edney,* University of Nottingham, UK*; E. Wilmot, J. Reid, J. Barker,* Innospec Ltd., UK*; M. Alexander, C. Snape, D. Scurr,* University of Nottingham, UK

Formation of insoluble fuel deposits in internal combustion engine components is a major problem for the automotive industry and the wider population. Their formation results in reduced engine efficiency and higher emissions of particulates and other toxic pollutants, contributing to accelerated global warming and reduced air quality. These issues constitute major crises from an environmental and healthcare perspective.

Characterisation of deposits is a necessary first step in mitigating their formation. Previous attempts have used a range of techniques, providing elemental and/or basic structural information.[1] Time of flight secondary ion mass spectrometry (ToF-SIMS) differs from other techniques and illustrated *in situ* analysis of deposits at all depths using a sputtering beam and first showed that deposits are layered materials. But the technique offers a relatively low mass resolving power (10,000) and only elucidated small molecular fragments due to its high energy ion beam (Bi_3^+, 25 keV). Thus, there is a need for further work to provide a comprehensive, molecular, characterization of deposits in 3D.

Here we introduce the application of 3D OrbiSIMS (HybridSIMS, IONTOF GmbH)[2], with its superior mass resolving power (> 240,000), for characterising gasoline and diesel engine deposits.[3] Single beam Ar_{3000}^+ (20 keV) depth profiles and chemical images with a resolution of 20 µm over a 280 μm^2 area were acquired. We identified diagnostic molecular fragments including high mass polyaromatic hydrocarbons such as circumovalene (*m/z* 812) and lubricating additive species such as alkyl sulfonates ($C_{18}H_{29}SO_3^-$) in deposits for the first time. Assignments were then confirmed using MS/MS. Depth profiling with chemical imaging at interfaces illustrated where key species were localised and gave insight into how the layered structure of deposits arises. Combined results elucidate previously unconfirmed sources of contamination in the fuel stream and inform the design of next generation fuel additives to prevent deposit formation in gasoline and diesel engines, helping to improve air quality and reduce the impact of global warming.

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AS-Contributed On Demand-121 Nano Gas Cells: Multimodal Surface Analysis of Catalytic Processes at Elevated Pressures and Temperatures*, Burcu Karagoz,* Brookhaven National Laboratory*; J. Carpena-Núñez,* Air Force Research Laboratory*; Y. Zhu, D. Zakharov,* Brookhaven National Laboratory*; B. Maruyama,* Air Force Research Laboratory*; D. Stacchiola, A. Head,* Brookhaven National Laboratory

Heterogeneous catalysis is usually analyzed by surface-sensitive techniques at ultra-high vacuum pressures and low temperatures using single crystals. However, catalysts used in industrial processes consist of metallic nanoparticles (NPs) and operate at near ambient pressures and high temperatures. To study heterogeneous catalysts in industrial conditions, we have developed nano gas cells. This cell allows studying solid-gas interfaces using anode-based ambient pressure X-ray photoelectron spectroscopy (APXPS) at temperatures up to 1300 °C and pressures exceeding the typical instrument limit of 10 mbar. This cell also enables multimodal transition electron microscopy (TEM) and APXPS experiments at pressures up to 1 mbar. We have tested the nano gas cell by covering DENS Solutions Wildfire nanochips with 100 nm Pd film with widely studied experiments such as CO adsorption/desorption reactions and Pd oxidation/reduction reactions. These known reactions confirm the gas cell temperature in the APXPS instrument. The growth of carbon nanotubes (CNTs) with metal oxide catalysts was also studied using both APXPS and TEM. This nano gas cell setup will be available to external users through the Center for Functional Nanomaterials (CFN) proposal system.

AS-Contributed On Demand-124 Plasma Modification of Lab Coat Fabrics for Improved Protective Clothing*, Kimberly Hiyoto,* *E. Fisher,* Colorado State University

With the widespread use of engineered nanomaterials in applications like healthcare, energy storage, sensing, and catalysis, secondary exposure from contaminated protective clothing is a major concern that is not widely studied.Although it is generally accepted that the fabric texture plays a vital role when determining nanoparticle (NP) adhesion and release on fabric, the impact of surface chemistry cannot be dismissed.Low temperature plasma treatment allows for the surface properties of the material to be tuned while the overall weave structure remains unchanged.This allows for direct comparison of the same fabric with differing surface properties to better elucidate how nanomaterials interact with these fabrics and if this behavior is influenced more by weave texture or surface chemistry.

Here, we describe plasma modification of four commercially available lab coat fabrics (100% cotton, polyester/cotton blend, polypropylene, and Tyvek®) and the resulting adhesion and release behavior with aluminum oxide NP, carbon black, and carbon nanotubes.Both C_3F_8 and $H_2O_{(v)}$ plasmas were used at relatively low applied powers to render the fabric more hydrophobic and hydrophilic, respectively.X-ray photoelectron spectroscopy indicates that C_3F_8 plasma treatment of all fabrics resulted in deposition of a thin fluorocarbon (FC) film with some contributions from the underlying material and $H_2O_{(v)}$ plasma treatment increased the amount of O on the surface by up to 10%.Contact angle goniometry confirmed the increase and decrease in hydrophobicity of the FC coated and $H_2O_{(v)}$ plasma treated samples, respectively when compared to the untreated material.Scanning electron microscopy images were used to characterize nanomaterial interaction following contamination and after vigorous shaking for both the untreated and plasma treated materials.With both the Al_2O_3 NP and the carbon black, the $H_2O_{(v)}$ plasma treated fabrics generally had the lowest initial attachment.In addition, differences between the untreated and plasma treated materials indicate the fabric texture is not the only property controlling NP adhesion and release.Results from imaging the same spot on some of the investigated fabric swatches (polypropylene and polyester/cotton blend) before and after shaking will also be discussed to directly demonstrate the potential for secondary exposure from these materials.Ultimately, better understanding of how nanomaterials interact with a variety of woven and nonwoven fabrics will allow for better safety recommendations and potentially designing more effective protective clothing.

AS-Contributed On Demand-127 Lab-Scale Hard X-Ray Photoelectron Spectroscopy (HAXPES): Application to Buried Interfaces in Device Technology*, **Pierre-Marie Deleuze**, E. Martinez, O. Renault,* CEA-Leti, France

X-ray Photoelectron Spectroscopy (XPS) is a powerful tool to study the electronic surface properties of materials. However, its low analysis depth remains a major limiting factor to study buried interfaces which properties are yet crucial in many applications. This limitation can be overcome using hard x-ray sources (HAXPES) thanks to the increase of the inelastic mean free path of electrons with increasing photon energy. Though HAXPES have been available at synchrotron facilities for many years, the recent advent of commercial laboratory instruments enables routine analysis with enhanced probing depth [1,2].

Here, we present the possibilities offered by a novel, Cr Kα (hv=5414.9 eV) lab-based HAXPES through several practical cases. In particular, we show that HAXPES can be appropriate to non-destructively probe buried interfaces in nanoelectronic devices. Among the examples, the potential of HAXPES is demonstrated through the investigation of Al_2O_3/GaN interfaces, which are of primary interest in the field of high-electron mobility transistors (HEMT). Results highlight that HAXPES is required to study realistic devices as the thickness of alumina plays important role on the structure properties. Furthermore, we discuss TiN/HfO_2 heterostructures intended for oxide-resistive random access memories (OxRAMs). The influence of a metallic Ti layer deposited at the interface is especially examined. Results reveal that the addition of a Ti layer promotes the reduction of hafnium oxide thus creating oxygen vacancies, which in turn greatly determine the device properties.

Acknowledgements:

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AS-Contributed On Demand-130 XPS Depth Profiling of Metal-Halide Perovskites*, C. Clark,* Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN 55455, USA.*; **Jennifer Mann**, B. Schmidt, K. Artyushkova, J. Newman,* Physical Electronics, Inc.*; E. Aydil,* New York University*; R. Holmes,* University of Minnesota,

The goal of an XPS depth profile is to obtain accurate identification of layer thicknesses and/or 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 [1-3].

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 [4-6].

Organo-metal-halide perovskites are of interest due their promising application in solar cells where they have achieved efficiencies above 25% [7]. In this work, we present XPS depth profiles of single films of different metal-halide perovskites having an ABX_3 structure(A = MA - methylammonium or Cs, B = Sn or Pb, X = Br or I). Depth profiles using all three sputtering guns available on the PHI *VersaProbe* III - monatomic Ar, C_{60} and argon gas cluster (GCIB) - were obtained to determine the viability of each gun in maintaining both the stoichiometry and chemistry of the film as it was sputtered.

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 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.

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AS-Contributed On Demand-133 Characterization on ALD-functionalized Magnesium Borohydride Materials for Hydrogen Storage*, **Margaret A. Fitzgerald**,* Colorado School of Mines, Department of Chemistry*; N. Leick,* National Renewable Energy Laboratory*; K. Gross,* H2 Technology Consulting LLC*; S. Christensen ,* National Renewable Energy Laboratory*; S. Pylypenko,* Colorado School of Mines, Department of Chemistry

Increasing energy demands and emissions require society to move towards more renewable and efficient energy carriers like hydrogen. However, development of effective methods of hydrogen storage and transportation is essential for the implementation of a hydrogen-based energy economy. Many materials can store hydrogen, including metal organic frameworks, activated carbons, and metal hydrides. Of these, metal borohydrides show promise as they have high gravimetric densities of hydrogen are potentially a more practical material for transportation[1]. One promising borohydride is magnesium borohydride ($Mg(BH_4)_2$, MBH), which with the addition of dopants (like titanium or fluorine),has potential to store hydrogen near room temperature at low-to-moderate pressures and at energy densities greater than either liquid or compressed hydrogen.[1] While MBH dopants are traditionally introduced mechanically, this work focuses on the characterization of MBH that has been doped using atomic layer deposition to introduce BN and TiN to tailor the deposited materials to a set of H2 storage targets. Understanding the complex chemical interactions between ALD precursors and the MBH requires a thorough characterization of the surface and bulk of as- received and ALD-functionalized materials. However, the air- and beam- sensitivity of MBH and particle heterogeneity of the as received and ALD-coated materials increases the challenges associated with characterization of this class of materials. This talk presents these challenges and presents the solutions developed in the characterization of the uncoated and coated MBH materials. Initial characterizations of these materials included temperature programmed desorption, surface area measurements, and scanning transmission electron microscopy (STEM) combined with energy dispersive X-ray spectrometry (EDS) are used to understand differences in the ALD-functionalized materials. Furthermore, ex-situ identical location STEM combined with EDS are employed to understand the effect of dehydrogenation on morphology and chemical composition of the materials. This allows to distinguish the heterogeneity of the initial materials from that of the deposited ALD coatings. Changes in morphology and composition are quantified and correlated to the amount of H2 dehydrogenation, the surface area, and H2 cyclability allowing for assessment of these materials in terms of performance and cyclability.

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AS-Contributed On Demand-136 Use of Artificial Intelligence Techniques to Automate the Analysis of XAFS spectra*, Jeff Terry,* Illinois Institute of Technology

One of the major issues affecting the scientific community is reproducibility[National Academies of Sciences, Engineering, and Medicine, \textit{Reproducibility and Replicability in Science}, 2019] or more specifically the lack thereof. A second issue involves the quantity of experimental data being produced on a yearly basis[C. Wang, U. Steiner, and A. Sepe, Small 14, 1802291, 2018]. Both of these issues limit the utility of the data collected during the operation of the synchrotron radiation user facilities. This hurts the scientific community as there is a strong possibility that important new science is lost, forever locked up in un-analyzed data that a funding agency paid to collect. Whether data is lost due to inactivity or was improperly analyzed, the knowledge that is lost cannot be used to improve our understanding of the physical world. At worst, time is wasted trying to replicate incorrect conclusions[M. Linford, V. Jain, and G. Major, AVS66 Abstract Book, 72, 2019]. Ultimately, there is a limit on what humans will be able to accomplish without the assistance of computers. Even with the efforts to train more experts, the amount of data that can be collected from *in situ* chemistry measurements exceeds what a researcher can analyze without computer assistance. We have developed an analysis program that reduces the amount of human intervention needed to successfully conduct the analysis of extended x-ray absorption fine structure (EXAFS) data.

There are three problematic issues that we have observed over the years in the analysis of EXAFS spectra. The first involves the data reduction involved to obtain the analyzable interference data, χ(k). The proper adjustment of the background parameters to reduce the contribution of low R (short scattering path lengths) is very confusing to novice users. Second, the extraction of local atomic structure from theoretical standards is difficult as it relies on human users to identify both the compounds and the respective scattering paths from each that are present in the experimental data. Third, the speed at which EXAFS data can be collected allows for *operando* monitoring of chemical reactions[G. T. Whiting, F. Meirer, and B. M. Weckhuysen, XAFS Techniques for Catalysts, Nanomaterials, and Surfaces, 167, 2016]. Our machine learning tools that we have developing can be used to address these problematic areas of XAFS analysis.

AS-Contributed On Demand-139 ALD Overcoating for Hydrogenation and Dehydrogenation Catalysts*, Staci Moulton,* Forge Nano

While ALD has grown to be an essential and widely implemented technique in two-dimensional nanoscale device manufacturing, the innovative commercial development of applications for three-dimensional and porous materials have comparatively lagged. At Forge Nano, we recognize the criticality of enabling these ALD-assisted technologies for commercial applications, particularly in catalysis. We will demonstrate that ALD-overcoated catalysts, adding a metal-oxide top layer to a traditionally fabricated catalyst, enabled metal catalysts through targeted coating strategies for specific catalytic deactivation challenges. Our overcoat catalysts retain activity, physical stability in hydrothermal and thermal conditions, achieve improvements in selectivity, and significantly enhance lifetime. For hydrogenation of muconic acid to adipic acid the Al_2O_3 ALD-coated catalysts retain up to two-fold activity for Pd on TiO_2 support. Second, the Pd leaching from the catalyst was reduced by four-fold on the ALD-coated catalyst. The same Pd on TiO_2 catalyst with ALD-overcoat showed significant resistance to physical restructuring under thermal treatment conditions shown both by STEM-EDS elemental mapping and activity data for uncoated and ALD-overcoated catalysts. Thermal treatment, or catalyst regeneration cycles, reduced the active catalyst surface area by over 80% for the uncoated catalyst while the ALD-overcoated catalyst retained all its active surface area over 5 regeneration cycles. The benefits of ALD for catalysis are proving to be a fertile working ground for both active materials and overcoat applications.

AS-Contributed On Demand-142 The Deterioration Mechanism of Silicone Elastomer during Vacuum Casting of Polyurethane*, Natalie Frese,* Bielefeld University, Germany*; M. Wortmann,* Bielefeld University of Applied Sciences, Germany*; K. Viertel,* Bielefeld University of Applied Sciences,, Germany*; W. Keil,* Paderborn University, Germany*; A. Welle,* Karlsruhe Institute of Technology, Germany*; W. Hachmann,* Bielefeld University, Germany*; C. Schmidt,* Paderborn University, Germany*; B. Hüsgen,* Bielefeld University of Applied Sciences, Germany*; A. Gölzhäuser,* Bielefeld University, Germany

The industrial production of prototypes made of polyurethane via silicone casting molds in the vacuum casting process is state of the art. The silicone molds show progressive deterioration, as the isocyanate component of the PUR casting resin diffuses into the silicone during processing, thus, limiting their service life [1]. Here, an in-depth investigation of the underlying chemical and physical mechanisms on a molecular level is presented. It has been shown that an anomalous diffusion process of diisocyanate into the silicone surface leads to the formation of interpenetrating polymer networks of polyurea derivatives in the poly(dimethylsiloxane) matrix [2]. The heterogeneous polymer system was examined in spatial resolution utilizing time-of-flight secondary ion mass spectrometry (ToF-SIMS), transmission electron microscopy (TEM), helium ion microscopy (HIM), atomic force microscopy (AFM), thermo-gravimetric analysis (TGA), X-ray photoelectron spectroscopy (XPS) as well as nuclear magnetic resonance spectroscopy (NMR).

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AS-Contributed On Demand-145 Oxidation of Amorphous Metal Alloy Surfaces Studied Using Ambient Pressure X-Ray Photoelectron Spectroscopy*, Pedro Alzaga,* Oregon State University and HP Inc.*; J. Diulus, R. Addou,* Oregon State University*; W. Stickle,* HP, Inc.*; J. Jenkins, G. Herman,* Oregon State University

Amorphous metal thin films (AMTFs) are of growing interest due to their unique mechanical properties and chemical stability. AMTFs have an advantage over polycrystalline metal films due to the lack of grain boundaries which gives AMTFs added durability and relatively smoother surfaces. For this reason, AMTFs have been investigated as potential materials for a wide range of applications such as protective layers in microelectromechanical systems, coatings for biomedical tools, and as metal-insulator-metal tunnel diode electrodes. However, AMTFs are known to be structurally and chemically unstable at higher temperatures and therefore the thermal stability of these materials need to be closely studied. The present research is focused on the characterization of the thermal stability of a ternary AMTF with a composition of $Ta_{54}W_{27}Si_{19}$ using ambient pressure X-ray photoelectron spectroscopy (AP-XPS). Using AP-XPS allows the composition and oxidation states of the growing oxide layer to be measured *in situ* as the AMTFs are heated in varying temperatures and O_2 partial pressures. Experiments were run at O_2 partial pressures ranging from 10^{-4} to 10 mbar and temperatures ranging from 25 to 300° C. Spectra have been obtained at a relatively short time intervals, which made it possible to determine the rate of oxide growth in combination with calculations using the Simulation of Electron Spectra for Surface Analysis (SESSA) software package. Analysis of the AP-XPS data indicated an increase in the apparent oxidation activation energy for $Ta_{54}W_{27}Si_{19}$ compared to similarly prepared polycrystalline tantalum films, which results in slower oxide growth. The results also indicated that the Ta in TaWSi films was preferentially oxidized, thus forming primarily a tantalum pentoxide (Ta_2O_5) layer on the surface.

AS-Contributed On Demand-148 High-Speed Analysis of Spectroscopic Ellipsometry Data Using Deep Learning Methods*, Yifei Li,* Massachusetts Institute of Technology*; H. Yu, I. Takeuchi,* University of Maryland, College Park*; R. Jaramillo,* Massachusetts Institute of Technology

As a high-precision and non-destructive measurement, ellipsometry is a powerful means to measure optical properties (*e.g.* refractive index) and characterize device processing (*e.g.* layer thickness). It would be particularly valuable in autonomous, closed-loop, high-throughput experimentation to develop new materials for integrated photonics. High-throughput experimental approaches require high-throughput data analysis methods to match, but ellipsometry data analysis using conventional machine learning (ML) methods of nonlinear regression is too slow. Solving the inverse problem of ellipsometry involves large numbers of parameters, but the parameter space and training time expand exponentially with the numbers of parameters. Hence, conventional ML methods make assumptions and compromise accuracy to reduce the number of parameters. This challenge is well addressed by deep learning (DL). The training efficiency of DL is exponential with the number of training data points, which counters the challenge of geometrically-large parameter spaces, making DL feasible in many cases for which conventional ML is infeasible. DL inference only involves matrix multiplication and a constant-time nonlinear function evaluation, which are orders-of-magnitude faster than nonlinear regression.

We construct and train a DL model to infer the optical properties of Ge-Sb-Te (GST) phase-change materials, deposited as thin films with a combinatorial composition gradients on SiO_2/Si substrates. In model testing, the mean-average-error (MAE) and standard deviation for the DL-inferred complex refractive index are 0.0329 and 0.0578 respectively. The DL method is five times more accurate than conventional human-directed non-linear fitting (benchmarked using simulated data), and 1,000 times faster (e.g. 700 ms vs. 30 min for analyzing experimental data from 177 unique compositions). We use DL ellipsometry to analyze the complex refractive index of 177 unique compositions in the GST system, and we and find that $Ge_{0.30}Sb_{0.27}Te_{0.43}$ has the optimal figure of merit for phase-change functionality in the 400-1000 nm wavelength range.

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AS-Contributed On Demand-151 Optimization of LLZCN/$LiPF_6$/PEO Solid-state Electrolyte for Energy Storage Application, ***Samuel Danquah,*** Norfolk State University; *C. Denize,* Norfolk Sate University; *J. Strimaitis, S. Pradhan, C. Bonner, M. Bahoura,* Norfolk State University

Solid-state electrolytes (SSEs) bring forth the chances to maximize the use of lithium metal anodes and intrinsically eliminate the safety concerns associated with flammable liquid electrolytes. The majority of SSE research has so far focused on increasing ionic conductivity and improving interfacial stability. Because ceramic electrolytes (LLCZN) have high conductivities but are fragile, and polymer electrolytes are easy to process but have low conductivities, we took the advantages of both by preparing a composite structure of these two materials. In this work, we investigate the effect of different proportions of the individual compounds towards the ionic conductivity, flexibility or both of composite solid-state electrolyte LLZCN/$LiPF_6$/PEO. Our results demonstrate significant progress towards all-solid-state electrolytes with good ionic conductivity for high-energy-density solid-state batteries. Furthermore, the electrochemical testing confirms that varying weight composition of the solid-state electrolyte has an effect on the cycling performance.

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AS-Contributed On Demand-157 Analysis of Thin Film Specimens Using ToF-SIMS Wedge Protocol, A Comparison with Depth Profiling, ***Vincent Smentkowski,*** *S. Goswami,* GE-GRC; *F. Kollmer, J. Zakel, H. Arlinghaus, D. Rading,* IONTOF GmbH, Germany

Depth profiling (1D or 3D) is often used to determine the depth distribution of species in thin films.An advantage of ToF-SIMS depth profiling is a full mass spectrum is saved at every volume element enabling 3D analysis of unexpected species; the analyst does not need to select the species at the start of the measurement.A disadvantage of ToF-SIMS depth profiling is the analyst needs to determine if they want to optimize the erosion and detection protocol for the collection of either the positive or negative ion fraction.MCs^+ analysis, where the region of interest is eroded using a Cs^+ ion beam and a Bi^+ cluster ion beam is used to perform positive ion analysis has been reported and enables the analysis of both positive ion (as Cs adducts) and negative ion (Cs_2 adduct) species in one depth profile measurement. Disadvantages of MCs^+ analysis include data complexity and for optimal performance, Xe/Cs co-sputtering is required.In 2011, Mao et.al. reported wedge sample preparation for ToF-SIMS analysis of thin layers using a home-built instrument [Dan Mao, Caiyan Lu, Nicholas Winograd, Andreas Wucher "Molecular Depth Profiling by Wedge Crater Beveling"; Anal. Chem. 83(16) (2011) 6410-6417doi:10.1021/ac201502w [https://dx.doi.org/10.1021%2Fac201502w]]; in 2018 IonTof added wedge preparation into their commercial instrument.

In this presentation we compare time of flight secondary ion mass spectrometry (ToF-SIMS) depth profiling of a multilayer thin film sample with ion images generated on a wedge cut.The benefits of both wedge preparation and multivariate statistical analysis (MVSA) are outlined.

AS-Contributed On Demand-160 Setting the Stage: Strain-Directed Metallization of Liquid Metals Using Surface Acoustic Wave Devices on Piezoelectric Substrates, ***Brian Rummel,*** *L. Miroshnik,* University of New Mexico; *A. Li, T. Sinno,* University of Pennsylvania; *G. Balakrishnan, S. Han,* University of New Mexico

In our previous work, surface acoustic wave (SAW) devices were fabricated on a GaAs (100) substrate to demonstrate the ability of Raman microscopy to image and characterize acoustic waves traveling on the surface of a piezoelectric substrate. We have adapted this research to study the effects of acoustic strain on the metallization of liquid indium on GaAs. SAWs are generated using a two-port interdigitated transducer (IDT) design, modified to produce standing waves within a 200 x 200 μm^2 window on the surface of the substrate. The standing SAWs produce surface stresses on the order 10^8 Pa. SEM/EDS analysis and AFM are used to characterize the diffusion behavior of the adatom species. Electrical device performance is recorded with a vector network analyzer, and surface displacements are measured with AFM and Raman microscopy. Experimental values are compared to simulations generated using COMSOL Multiphysics. Furthermore, we show preliminary results demonstrating the potential of increasingly complex IDT geometries to produce intricate diffusion patterns for quantum structures or single electron device fabrication.

AS-Contributed On Demand-163 Current Trends in XPS Data Analysis, Including Major Errors and the Most Common Elements and Materials Analyzed, ***George Major,*** Brigham Young University; *T. Avval, B. Moeini,* Brigham Young University; *A. Herrera Gomez,* CINVESTAV-Unidad Querétaro, México; *C. Easton, T. Gengenbach,* CSIRO, Australia; *W. Skinner,* Future Industries Institute, University of South Australia, Australia; *D. Baer,* Pacific Northwest National Laboratory; *M. Linford,* Brigham Young University

X-ray photoelectron spectroscopy (XPS) is the most widely used method for chemically analyzing surfaces, with applications in numerous areas of research and technology. In part, the popularity of XPS is due to the large amount of chemical information it derives from the surface, including chemical compositions, chemical and electronic states of elements, and elemental bonding. Extraction of this information, however, is not always straightforward. Various articles and guides have recently been published that teach and illustrate good methods for interpreting and fitting XPS data. In conjunction with these guides, some of us have recently surveyed 407 publications from three major journals that show XPS to gain greater insight into how XPS is being used, e.g., whether there are mistakes or errors in XPS analysis, which elements are the most commonly fitted, and which are the most problematic. A committee of international experts was formed to review the peak fitting in these papers and to rank the results vis-à-vis a list of common errors in XPS peak fitting. Error classification ranged from minor errors that have little impact on the interpretation of the results, such as plotting the spectrum against convention (with binding energy increasing to the right), to major errors that call into question the interpretation of the data or even of the entire study, such as not properly constraining the full-width half maxima values of fit component peaks. We found that 65% of the publications we analyzed included fitted XPS data. Of this fitted data, 40% showed major errors. The most popular elements that were fitted/shown are carbon, oxygen, nitrogen, sulfur, and titanium. In the papers we reviewed, the most common form of carbon (C 1s) that is analyzed is sp^2 carbon, and the most common form of oxygen (O 1s) that is analyzed is from inorganic oxides. These findings should help guide and direct further efforts for new XPS tutorial material.

Applied Surface Science Division
Room On Demand - Session AS-Invited On Demand
Applied Surface Science Invited On Demand Session

AS-Invited On Demand-1 Hard Targets: Developing Tools for Quantitative HAXPES*, David Cant,* National Physical Laboratory, U.K. **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 placed in the development of tools such as sensitivity factors, transmission calibration procedures, parameter databases, simulation software, interpretation formulae, and more. Thanks to such tools, the results 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, typically, the top ~10 nm of material. Nevertheless, sometimes 10 nm is not enough.

Until recently, photoelectron spectroscopy 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 trials and tribulations, as well as ruining a perfectly good sample, while the latter introduces a plethora of complexities which render calibration difficult, and careful experimental design and reference materials a necessity. However, recent developments in the design of instruments utilising higher-energy, or 'hard' x-ray anodes have begun to make synchrotron-energy XPS instruments more readily available in the lab. This will allow more analysis of samples that previously might have been restricted to synchrotron studies; for example in non-destructive depth-profiling of coated samples such as core-shell nanoparticles, particularly those with shells 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 a spectrum that stretches some KeV beyond, and relative sensitivity factors for each new photon energy are needed, particularly given the cornucopia of new core levels made available and the increased breadth of sensitivity at higher photon energies.

Here we discuss developments towards more trustworthy, quantifiable XPS and HAXPES measurements.The development of theoretical sensitivity factors for silver and gallium x-ray sources is described, as well as demonstrating their validity in depth-profiling of samples well beyond the depth achieved by aluminium. 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 HAXPES systems at a range of energies is proposed.

AS-Invited On Demand-19 ASSD 2020 Peter M.A. Sherwood Mid-Career Professional Award Talk: Innovations in Biological, Nanoscale, and Nuclear Materials Analysis with SIMS*, Christopher Szakal,* National Institue of Standards and Technology **INVITED**

This presentation will highlight advances in secondary ion mass spectrometry (SIMS) to address measurement gaps in the characterization of biological, nanoscale, and nuclear materials as related to the 2020 Peter M.A. Sherwood Mid-career Professional Award. Presented work will focus on the development of methods needed to answer questions related to single cells, nanomaterial surface chemistry, and micrometer-sized actinide particles. Despite the wide range of applications, these are distinct examples of how time-of-flight (TOF)-SIMS and large geometry (LG) magnetic sector SIMS can add value to multiple scientific fields.

AS-Invited On Demand-25 The Role of Photoelectron Diffraction Effects on the Flat Surface State Bands Close to the Fermi Level: Revisiting the Si(111) 7x7 Surfaces*, María C. Asensio,* Materials Science Institute of Madrid (ICMM), Spanish Scientific Research Council (CSIC), Spain **INVITED**

Lately, seminar discoveries of new surface states of matter have been reported almost every year, disclosing new materials such as topological insulators and superconductors, high-temperature superconductivity in hydrates under pressure and pnictides, and a large diversity of many-body phases in the flat bands of Moire lattices of a few atomic layers of two-dimensional materials. The continuing search for higher degrees of miniaturisation and the rise of new quantum layer materials such as silicene, graphene, and topological matter, drives an accruing need to understand the electronic structure of systems dominated by surface states confined just in a few atomic layers. The unconventional evolution of the electronic properties of reducing material to a few-layer plays a central role in microelectronic devices silicon technology. Moreover, unravelling the peculiar attributes of the electronic properties of the upper layers of silicon with their characteristic two surface state bands may have a remarkable impact on the transport properties of silicon-based nano-devices that are crucial for future high-speed electronics nanotechnologies.

In this presentation, the role of localisation of typical surface state bands of the 7x7 reconstructed surfaces of silicon will be revised. In particular, the metallic character of the surface bands close to the Fermi level will be investigated, taking into account the influence of photo-diffraction effects on the Fermi surface topology measured using Angle-resolved photoemission spectroscopy (ARPES). In contrast to previous studies, our findings show that the two-dimensional intensity patterns at constant energy close to the Fermi level are due to strong photo-diffraction effects modulated by the photoemission matrix element, instead due to the Fermi level crossing of the metallic delocalised surface states bands of the outmost surface state of the (7x7) reconstruction. Combining ARPES experiments and multiple scattering calculations, our results unravel a comprehensive understanding of the orbital character of the adatoms and rest-atoms in terms of a remarkable atomic localization of the Si (111) 7x7 reconstructed surface state bands lying at the silicon bulk gap.

AS-Invited On Demand-37 Hardware and Data Analysis Methods for Integrating TEM and Atom Probe Tomography*, Brian Gorman,* *E. Supple, G. Burton,* Colorado School of Mines **INVITED**

Errors during APT data reconstruction are still limiting widespread acceptance of APT as a quantitative imaging technique. There are many factors contributing to these reconstruction inaccuracies, but they include empirical estimation of specimen geometry based upon the assumed evaporation field, inaccurate assumptions of the ion trajectories, and magnification changes due to varying field evaporation characteristics at heterointerfaces. Utilizing ex-situ correlative TEM imaging with APT has been shown to improve the accuracy of data reconstruction through the quantification of many of the reconstruction variables, including radius, shank angle, atomic spacing, detection efficiency, image compression factor, and field of view. However, the full use of TEM has not yet been applied to the APT experiment as a wealth of other information are useful and readily attainable. In order to further improve APT as a quantitative imaging and analysis technique, hardware enabling in-situ APT within a TEM objective lens is needed. Our hardware solution enables APT within a TEM objective lens using a modest investment of capital hardware. UHV is obtained using a combination of turbomolecular pumping and a cryogenic trap within the TEM pole gap. Cryogenic specimen temperatures are achieved using a recirculating cryocooler with vacuum transfer to both the side entry stage and the objective lens cryo trap. A commercially available large field of view delay line ion detector assembly fit to a UHV flange is engineered to bolt on the TEM column opposite the specimen holder. Laser integration with commercial in-situ TEM hardware are currently available and being utilized for this instrument. 4-D STEM datasets are utilized in a correlative manner for quantification of the specimen function before the field evaporation experiment. The specimen function contains the real space volume and atom positions (determined from reciprocal space) and can subsequently be created and sliced perpendicular to the evaporation axis. Comparing the specimen function with ion field evaporation maps from the correlative APT experiment in Fourier space allow for quantification of aberrations during the field evaporation experiment. As such, APT may one day become a simple addition to existing electron microscopy hardware.

AS-Invited On Demand-43 High Resolution Angle-Resolved Photoemission Spectroscopy Studies of Quantum Materials*, Inna Vishik,* University of California at Davis **INVITED**

Quantum materials are unified by the theme of emergence, whereby the properties of a many-electron system differ from a single-particle description.They often exhibit surprising electronic behavior that is readily revealed by angle-resolved photoemission spectroscopy (ARPES).In this talk, I will discuss recent results on superconducting and topological quantum materials which exemplify how novel materials platforms conspire with this powerful experimental technology to elucidate both new and long-standing problems in this field.

AS-Invited On Demand-55 Synergies between Synchrotron and Lab-Based X-Ray Techniques for the Studies of Complex Materials and Interfaces*, Alexander Gray,* Temple University **INVITED**

The several recent studies discussed in this talk were motivated by the challenge of creating new strategies for rational design and control of electronic and magnetic phases of matter at interfaces. The key requirement for the realization of such groundbreaking technology is a clear understanding of how these electronic and magnetic phases arise and evolve at the nanoscale. Gaining such an understanding is not just important for basic science but could be potentially transformative to modern computing. The depth-sensitive synchrotron and lab-based x-ray photoemission techniques developed in the Fadley Group helped elucidate such important phenomena as metal-insulator transitions [1], two-dimensional electron gas [2], and interfacial magnetism [3]. Here, I will discuss several recent studies stemming from this seminal body of work and taking full advantage of multiple complementary x-ray spectroscopic and scattering techniques to probe emergent electronic phenomena at oxide interfaces [3-6].

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.

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Biomaterial Interfaces Division
Room On Demand - Session BI-Contributed On Demand

Biomaterial Interfaces Contributed On Demand Session

BI-Contributed On Demand-1 A Mussel Inspired Catechol Polymer: Is It Sticky?*, **Laura Mears**, J. Appenroth, M. Valtiner,* Vienna University of Technology, Austria

Mussel foot proteins are an inspiring material for adhesives that can work in challenging, saline environments. There has been a focus on the high concentration of L-DOPA within the proteins believed to be the source of strong adhesion. The nature of catechols in general provides for both interactions of the aromatic group and the hydroxyl groups for hydrogen bonding with surfaces. The carboxylic acid groups on amino acids like L-DOPA make these molecules particularly sensitive to the pH of the environment, which the mussel appears to exploit to regulate their adhesive interaction. The catechols are also active electrochemically, expanding the methods that can be used to control their interactions.

Here, we will present work on a catechol based polymer. The adhesive properties have been tested using the surface forces apparatus, a force sensitive technique, which uses multiple beam interferometry to track the confined thickness of the material. The polymer was confined between various surfaces in order understand its adhesion, also in a range of electrolyte environments (salt concentration, pH etc.) to mimic real world conditions. The results will be put into the context with the performance of biocompatible adhesives, with a particular view to medical and biomedical engineering applications that present these challenging saline environments in the real world.

BI-Contributed On Demand-4 Fast, Accurate Blood Analysis Algorithm for X-Ray Fluorescence on Homogeneous Thin Solid Films of Microliter-sized Whole Blood Droplets*, T. Balasooriya, W. Peng, N. Suresh, A. Gurijala, S. Khanna, A. Chow, M. Sahal,* Arizona State University*; S. Ram,* Yale University*; S. Narayan,* University of Pennsylvania*; Y. Pershad,* Stanford University*; E. Culbertson,* Ronald Reagan UCLA Medical Center*; R. Culbertson, N. Herbots,* Arizona State University*; V. Desai, **Aarush Thinakaran**,* MicroDrop Diagnostics, LLC

Whole blood diagnostics use High-Performance Liquid Chromatography (HPLC), requiring hours to days for analysis of 2-10 mL blood volumes. Small volume, fast blood tests, e.g. glucose monitors, yield results in seconds but are limited to a single blood component.

Fast, accurate whole blood tests are necessary for medical practices, ER, OR, ICU/NICU, etc. to monitor patient status for electrolytes, and many other conditions.

This work tests a radical new approach to not only reduce blood volumes drawn but also to yield faster and highly accurate whole blood diagnostics for several elements. Super/hyper-hydrophilic coatings HemaDrop™ can rapidly solidify µL drops into planar Homogenous Thin Solid Films (HTSFs)[1,2]in minutes. HTSFs can be formed by applying blood drops on a strip coated with HemaDrop with metered calibration and analyzed by XRF or other solid state methods. XRF data collection takes minutes compared to HPLC, counting X-Rays at a high data rate instead of hours-long microfluidics of blood in porous ceramic columns. XRF analysis software is not accurate enough for medical standards, which requires relative error <10%. XRF analysis software typically uses an all peaks fitting algorithm while searching fits with 117 of the 118 elements of theperiodic table.

Most XRF software fits the whole spectra with polynomials, yielding false positives for detection, and significant error (> 50%) due to background distortion around small signals from trace elements, which are of key importance in blood diagnostics. Finally, XRF emission lines, being neither Gaussians nor Lorentzians, are ill-suited for curve fitting. To improve speed, accuracy and reliability of XRF on blood HTSFs, a new algorithm, “Fast, Accurate Blood Analysis by XRF” (FABAX), is coded as an app, “Fast, Hand-Held Analysis by XRF”(FHAX) . FABAX computes a Riemann sum of counts across the full signal width for each tagged element and subtracts a trapezoidal sum computed from background noise levels left and right of the signal, instead of a potentially poor or error-laden fit.

FABAX interfaces with handheld XRF analyzers or desktop XRF units via smartphone, to generate fast, accurate, reliable blood diagnostics. Small footprint, handheld XRF units combined with a smartphone are suited to space limitations typical of medical settings. Crammed OR’s, crowded ER patient triage stations, or refugee camps can use it quickly and accurately to determine blood electrolytes and metal in mg/dL, using the built-in triple calibration, from one 10 µL blood drop.

[1] N. Herbots, et al. (2019). MRS Advances. 1-25. 10.1557/adv.2019.398.

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BI-Contributed On Demand-10 Surface Analysis of Alum Adjuvant for Vaccine Development and Delivery*, G. Guerrini,* University of Siena LAMMB (Biotechnology and Molecular Microbiology Lab), Italy*; J. Banuls Ciscar,* European Commission, Joint Research Centre, Italy*; F. Fumagalli,* European Commission, Joint Research Centre, Italy*; J. Ponti, L. Calzolai,* European Commission, Joint Research Centre, Italy*; D. Medaglini,* University of Siena, LAMMB (Biotechnology and Molecular Microbiology Laboratory), Italy*; **Giacomo Ceccone**,* European Commission, Joint Research Centre, Italy

The worldwide pandemic crisis caused by the COVID 19 virus strongly impact almost all human activities. In absence of a specific pharmaceutical products and vaccine, virologists and medical experts agree that the only way to fight and reduce the risk of infection is to maintain the physical distance while tracing the positives cases and impose quarantine in places where the infecting parameter R_0increases above 1. However, this type of measures impacts dramatically the economic situation and the research to find a vaccine has become extremely urgent.

The development of vaccine is not an easy task especially when pure antigens are employed for reducing vaccine immunogenicity. This requires the use of adjuvants to optimize vaccine effects whilst maintaining its safety.

Adjuvants based on Aluminium salts are amongst the most used because of its high safety profile, whilst its mechanisms of actions still remain unclear.[1,2,3]

In this work we present a detailed surface analysis by means of X-ray Photoemission Spectroscopy (XPS and Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS) of a polymeric platform to be used for vaccine development and delivery. This platform consisted in Al containing polymer substrate prepared in two different formulations, namely micro-Alum and nano-Alum. The effectiveness of the Alum-platform was tested against ovalbumin protein.

Both XPS and ToF-SIMS were able to deliver information about the interaction of the ovalbumin and the substrate. In particular, results indicate that, independently of the substrate formulation (micro or nano), a ratio of Alum/OVA of 3:1 was required to reach saturation, confirmed on sample superrnatant by SDS-PAGE gel, where the 3:1 ratio is the first in which OVA protein could be detected.

Moreover, Circular dichroism analysis on Al:OVA complexes shown a conformational change of the protein secondary structure upon adjuvant binding

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BI-Contributed On Demand-13 Design for X-ray Fluorescence, X-ray Photoelectron Spectroscopy, and Ion Beam Analysis of Blood Drops solidified as Homogeneous Thin Films for Fast, Small Volume, Accurate Diagnostics*, N. Suresh, A. Gurijala, S. Khanna, A. Chow, W. Peng, T. Balasooriya,* MicroDrop Diagnostics, LLC*; M. Sahal,* Arizona State University*; L. Puglisi,* SiO2 Innovates, LLC*; E. Culbertson,* MicroDrop Diagnostics, LLC*; N. Herbots,* Arizona State University*; A. Thinakaran, **Ashwin Suresh,*** MicroDrop Diagnostics, LLC

Analysis in the liquid phase for blood diagnostics requires 2-10 mL volumes to reach the medical accuracy standard, relative errors < 10%.

Assessing/monitoring patients requires fast diagnostics for blood such as electrolyte (Na, Mg, K, Cl, Fe), O2 levels, total proteins, CO2, metals (e.g. Pb), and radio-nuclides (e.g, Co^{60}). Tests may need repeating hourly or daily in ICUs. But drawing mLs of blood results in Hospital-Acquired Anemia for premature infants in NICU, patients in ICU and the chronically ill. Small blood volume diagnostics (SBVD) is key to improve care.

A rapid SBVD thin film device, InnovaStrip™[1-4], has been designed to process µL-sized blood drops into uniform, uncoagulated, thin solid films for analysis the solid state rather than liquid, via hyper-hydrophilic coatings, called 'HemaDrop™ WB'[1-4]. Super-hydrophilic coatings 'called HemaDrop™ P'[1-5] can also separate plasma and serum for more detailed diagnostics.

HemaDrop™ coated InnovaStrip devices are designed to solidify µL-blood drops into Homogeneous Thin Solid Films (HTSFs) rapidly and consistently by absorbing in less than 5 minutes the aqueous component of whole blood in a temperature range of 18-25°C and relative humidity ranging from 25-50%.

Ion Beam Analysis (IBA) and X-Ray Fluorescence (XRF) of whole blood and plasma HTSF can yield accurate Na, K, Mg, Ca, Cl and Fe composition with relative errors < 10% in less than 20 min from blood drop collection to diagnosis[5].

InnovaStrip™ consists of Al-clad substrates coated with HemaDrop™ with wells for drop collection into HTSF, and calibrated solutions HTSF for conversion of a/o into mg/dL.

Based on IBA, XRF and XPS compositions from different depths, the thickness of blood HTSF, HemaDrop coatings and metal cladding are optimized for reproducibility and accuracy to medical standards < 10%.

HTSF uniformity is measured via optical microscopy and XPS. XPS probes HTSF composition to within an escape depth of 5 nm. XRF is fast, compact and portable, and conducted in air, ideal for SVBD in the ER, OR, MD office, field hospital or crisis area.

IBA and XRF reach < 2-3% relative error, and are reproducible to ≤10% using InnovaStrip™ µL-sized whole blood drops and blood plasma can be uniformly solidified into thin solid films and analyzed in the solid state in air and in vacuo for composition. The advantages of SVBD in the solid state include speed, accuracy, ease of storage, reduced risk of contamination, while maintaining accuracy.

[1-4] N. Herbots, N. Suresh et al. US & Intl. Pat. pend (2016-20).

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BI-Contributed On Demand-16 Mussel Foot Adhesion: A Fundamental Perspective on Factors Governing Strong Underwater Adhesion*, J. Appenroth, L. Mears, P. Bilotto, A. Imre, H. Cheng, **Markus Valtiner,*** Vienna University of Technology, Austria

Tuning interfacial electrochemistry is central to the principle of the strong underwater adhesive of mussels. In this contribution 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.

Specifically, we will show electrochemical signatures of a large number of different catechol functionalities and show how catechol chemistry can be utilized for cross-linking musselfoot mimicking polymers. Further, we will show how the electrochemical oxidation of catechols can steer the interfacial ion concentrations by a variation of the pH value, and hence surface charging. We can correlate this with interfacial interaction forces measured by AFM and the surface forces apparatus.

In this view we will discuss paths into further understanding and utilizing redox-proteins and derived polymers for enhancing underwater adhesion in a complex salt environment.

BI-Contributed On Demand-19 Hand-Held X-ray Fluorescence (XRF) Analysis for Fast, Accurate, Comprehensive Small Volume Blood Diagnostics using Blood Drops Rapidly Solidified into Homogeneous Thin Solid Films*, **Thilina Balasooriya**, W. Peng, N. Suresh, A. Gurijala, M. Sahal,* Arizona State University*; S. Narayan,* University of Pennsylvania*; Y. Pershad,* Stanford University*; E. Culbertson,* UCLA Medical Center*; R. Culbertson, N. Herbots,* Arizona State University

Over 4 billion Blood Diagnostics (BD) tests are performed annually worldwide. Current diagnostics uses High-Performance Liquid Chromatography (HPLC). HPLC requires hours to days for results and uses 2-10 mL of blood. Drawing tens of mL of blood for multiple tests leads to hospital-acquired anemia at a rate of 74% in the chronically ill. Faster and more comprehensive whole blood tests are needed in ERs, ORs, and ICUs to diagnose incoming patients immediately for dehydration, anemia, etc.

This work investigates a new approach via a new hand-held device design - called InnovaStrip™ - to greatly reduce blood volumes for BD. InnovaStrip™ yields *simultaneously* more accurate and *comprehensive* BD for electrolytes (Na, Mg, Ca, Cl, K, Ca), metals (Fe, Cu, Se, I), toxins (As, Cd, Hg, Pb), and radio-nuclides (^{87}Sr, ^{131}I, ^{235}U, ^{239} Pu) and aims to diagnose presenting conditions at intake with one *single initial* Small Volume Blood Diagnostics (SVBD) test, instead of several, within minutes.

InnovaStrip™ includes three components: (1) low-cost blood drop collection strips, (2) a hand-held X-Ray Fluorescence (XRF) analyzer and (3) an innovative SVBD algorithm, '*Fast Accurate Blood Analysis*, or FABA™, deployed via an app, '*Fast Hand-held Analysis for XRF*', or FHAX™. The blood collection strips, made of off-the-shelf components, are coated with a new Hyper-Hydrophilic coating, 'HH HemaDrop™'. These coatings rapidly planarize and solidify µLs of blood into Homogenous Thin Solid Films (HTSFs) in minutes. The collection strips include three HSTFs of pre-solidified calibration solutions for rapid conversion of XRF relative concentrations into medical units of mg/dL for BD. Besides XRF, other solid-state analyses such as Ion Beam Analysis via compact ion sources like ^{241}Am can be incorporated in the analyzer.

The medical 'gold' standard for SVBD - such as blood glucose monitors - requires relative errors ≤ +/-10%, in other words, less than 10% false negatives or positives. Current XRF analysis commercial software is not accurate for trace elements such as blood electrolytes. They have poor background fitting, yield false positives/negatives, and yield large errors (> 50%) for trace elements quantitation. Instead, FABA™ computes fast, direct Riemann sums of counts for raw signals of selected elements *only* and subtracts the *actual* background, and is optimized for each specific element, instead of using an all-encompassing curve fit. FABA then interfaces with handheld XRF analyzers via the FABA App to generate accurate BD results. ORs, ERs, refugee camps, and other medical settings can use InnovaStrip™ to quickly and accurately diagnose initial patient status for blood electrolytes and iron – thus hydration and anemia – from one single 10 µL blood drop.

BI-Contributed On Demand-22 GCIB-ToF-SIMS Imaging for Lipid Imaging in Planaria*, **Lara Gamble**, D. Graham,* University of Washington, Seattle*; C. Anderton, D. Velickovic,* Pacific Northwest National Laboratory*; T. Angerer,* University of Washington, Seattle

Lipids not only make up the structure of cells walls, they have also been recognized as key players in cell signaling and disease. Information on their location and their changing distribution under different conditions can result in a better understanding of individual lipid species contributions to changes in phenotype. In order to map the lipidomic landscape in planarian worms, longitudinal sections of planaria were analyzed with imaging time-of-flight secondary ion mass spectrometry (ToF-SIMS). The data contained in the resulting images were analyzed with multivariate analysis (MVA) in order to identify chemically unique areas in scores images as well as the mass spectrometry (MS) signals (peaks) associated with those areas in loading plots. By comparing light microscopy images of the sections and MS/MVA scores-images, we were able to identify several organ structures in the sections: brain (CNS), intestines, pharynges (different to other planarian species, *Phagocata gracilis* has multiple small pharynges instead of one central pharynx), testes, and several parts of the male reproductive system. Subsequently, we were able to identify unique lipid species present in each organ system. The lipid assignments, respective fragment identities, and their locations from ToF-SIMS analysis were confirmed via LC-MS/MS on lipid extracts and ultra-high mass resolution MALDI-MS imaging. It was found that for many lipid species, the fragmentation patterns within ToF-SIMS spectra match those seen in MS/MS. These data show that the semi-destructive nature of ToF-SIMS can be utilized to enable more confident molecular annotation by providing intact molecular species and their fragments simultaneously.

BI-Contributed On Demand-25 Studying the Aggregation Effect of Microbes on Mineral Oxide and Synthetic Soil Using ToF–SIMS*, **Yuchen Zhang**, X. Yu, J. Son,* Pacific Northwest National Laboratory*; Q. Huang, W. Chen,* Huazhong Agricultural University, China

The colonization of bacteria and the subsequent formation of biofilms on mineral surfaces play a key role in soil aggregation and organic processing. Therefore, characterization and understanding of the biofilm interactions with soil components are important in deepening our knowledge in the biosphere and rhizosphere. In this work, *Shewanella* MR-1 was used as the model bacteria biofilm due to its known traits in soil chemistry and microbiology. A mixture of silica, alumina, and iron oxide was used as the model soil system. A microfluidic chamber was developed to culture biofilms using soft lithography and polydimethylsiloxane. The infrastructure of the microchamber was largely based on the system for analysis at the liquid vacuum interface, or SALVI. Specifically, a clean silicon (Si) wafer was included as the main substrate for biofilm attachment in the microfluidic chamber for fast prototyping and bacteria screening. When the mature biofilm formed in the micro channel, the soil component was mixed to the growth media (TSB without dextrose) and used as nutrients to support the biofilm's growth. The effluent was collected periodically after 0, 4, 8, 12, 16, 24 and 48 hours (hr.) to follow the evolution of the mineral and microbial interactions. Samples were desalinized and deposited onto the Si wafer prior to using time-of-flight secondary ion mass spectrometry (ToF-SIMS) for further analysis. ToF-SIMS is a sensitive surface technique and it offers submicrometer spatial mapping of molecular species of importance in metabolic processes compared to other mass spectrometry techniques. Our initial results show that a significant transition point of compositional changes occurs between 4 and 8 hr. In addition, new peaks such as fatty acids and lipid fragments appear in the biofilms and the mineral oxide mixture compared with controls of bacteria biofilms and planktonic cells, respectively. Interestingly, clusters of organic fragment peaks appear frequently in the high mass range, i.e., $m/z > 500$, after interacting the biofilm and minerals, suggesting the formation of new extracellular polymeric substance (EPS). We postulate that these high mass peaks are lipids, proteins or polysaccharide components. Peak identification is in progress. Additionally, the formation of these new substances may be related to biomineralization process as a result of the interaction of the biofilm and soil mineral components. Integration of the microfluidics and ToF-SIMS provides a new approach to study the interaction between biofilm and soil simulant, taking advantage of the ToF-SIMS high resolution mass spectral analysis and the ability of following the living bacteria behavior inherent of microfluidics with sensitivity and selectivity. Our new findings provide new insights into the role of biofilms in soil aggregation that occurs at the microbe-mineral interface.

BI-Contributed On Demand-28 Toward Custom Degradation of Silk-Based Biomaterials: Tailoring the Surface Chemistry of Silk Fibroin via Plasma-Based Strategies*, **Morgan Hawker**,* California State University, Fresno

Naturally-derived, degradable polymers offer tremendous potential to the field of biomaterials. Indeed, the presence of degradable devices in pre-clinical/clinical trials and on the market has expanded considerably over the past decade, spanning a variety of applications from stents to suturing. Degradable devices are designed to perform their intended function for a set time, after which they break down into harmless byproducts. These byproducts are then absorbed by the body, mitigating the need for secondary removal surgery. Notably, degradable polymeric devices are typically designed for a specific application and, thus, exhibit fixed degradation kinetics. Furthermore, prior attempts to control naturally-derived polymer degradation used methods that altered the polymer's bulk mechanical properties (e.g., physical cross-linking), which can hinder the device function due to mechanical mismatch between the device and its surrounding biological environment. There is a critical need to develop a fabrication technology that results in polymeric devices with programmable degradation rates - without altering their bulk mechanical properties - for deployment over a range of intended applications.

This talk will highlight recent efforts to develop a radio-frequency plasma copolymerization approach with the potential to modulate the degradation of naturally-derived polymer materials. In this work, silk fibroin (SF) was used as a model polymer system. Naturally-derived polymers like SF are known to degrade via surface-mediated enzymatic hydrolysis, so surface properties are paramount in controlling polymer construct/enzyme interactions. As such, the objective of this work was to prepare SF films with variable surface properties. SF films were first dropcasted using established methods, and films were subjected to plasma treatment to customize their surface chemistries/wettabilities. Plasma feedgas composition was tuned using two unique precursors: 100% acrylic acid (to produce thin films with polar functional groups on the SF surface), 100% pentane (to produce thin films with non-polar functional groups on the SF surface), and mixed precursor conditions (to create SF surfaces with intermediate wettabilities). Plasma parameters were optimized for each individual precursor, as well as for copolymerization. Contact angle goniometry was utilized to evaluate the wettability of all plasma-modified and control SF films. Findings demonstrated that surface wettability depends not only on feedgas composition, but also on applied plasma power. Collectively, this plasma copolymerization strategy is a promising method to customize naturally-derived polymer degradation.

BI-Contributed On Demand-31 Using Transferrable Graphene-Based Membranes for Spatial and Temporal Control of Cell Cultures*, **Keith Whitener**, D. Haridas, W. Lee,* US Naval Research Laboratory*; S. Yoseph,* Howard University*; C. So, J. Robinson,* US Naval Research Laboratory

Exerting spatial and temporal control over cell populations is a powerful capability which offers the promise of manipulating and interrogating living systems for use in advanced biological engineering such as bottom-up tissue engineering. To this end, we have developed techniques for reversibly transferring graphene-based thin film materials in a biocompatible way. Using single-layer hydrogenated graphene as well as partially reduced graphene oxide as mechanical support layers, we can deposit spatially patterned materials such as metallic electrical contacts, molecules with biochemical activity, and polymers, and transfer them to arbitrary surfaces using simple water delamination. We found that incorporating a thin gelatin layer onto the film mitigates cytotoxicity and cytolysis associated with graphene-based materials and enables transfer of materials-patterned thin films to mesenchymal stem cells without sacrificing viability. In addition, the low melting point of gelatin enables facile removal of these thin films. Simple and fast fabrication, deposition, and removal of patterned materials on cells allows for spatial as well as temporal control over external stimulus delivery to those cells. We also found that the partially reduced graphene oxide thin films are impermeable to most molecules, and we are exploiting this property along with transferrable photolithography to construct cell masks for spatially patterned biomolecule delivery and cell cocultures.

BI-Contributed On Demand-34 Polymeric Thin Films Designed to Direct *Pseudomonas aeruginosa* Iron Scavenging, Biofilm Growth, and Pathogenicity*, **Trevor Donadt**, Y. Wu, J. Lang, S. Li, R. Yang,* Cornell University

Ample biointerfacial materials research has focused on biocidal or antifouling outcomes, yet some microbes can be utilized for advantageous qualities when allowed to colonize a surface under appropriate conditions. A critical bottleneck has formed in the design and deployment of functional yet safe microbes due to a small selection of materials that have been used to both support growth and program microbial function without genetic manipulation. Our approach to programming microbial function involves the use of initiated chemical vapor deposition (iCVD) to design polymer thin film coatings with properties that control the behavior of exposed bacteria. The present work examines iCVD-generated polymer thin films that behave cooperatively in iron scavenging by *Pseudomonas aeruginosa* and change the expression of siderophores and biofilm formation by cells cultured on these films, resulting in reduced virulence. The material characterized herein sets the stage for future work on tunable biointerfaces that influence microbial activity exclusively through surface phenomena without reliance on soluble elements.

BI-Contributed On Demand-37 Hydrogen Peroxide Detection Using Modified Electrochemical Electrodes for the Intestinal Environment*, **Santiago Botasini**, D. Jesner, J. Stine, R. Ghodssi,* University of Maryland

Electrochemical hydrogen peroxide (H_2O_2) sensors have been extensively researched using enzymatic and non-enzymatic approaches. The last one is most promising as they not suffer from enzyme denaturalization. However, their application in real environments is limited due to matrix interference. In particular, H_2O_2 and other reactive oxygen species (ROS) have been linked to bacterial recognition responses and autophagy within the human gastrointestinal tract (GIT), and are related to inflammasome activation. In the gut, high concentrations have also been correlated with the presence of epithelium inflammation. This could be due to circumstantial internal illness but could also be indicative of a degradation of mucosal permeability, which has been hypothesized as the primary cause of several chronic autoimmune pathologies, such as Crohn's disease, type-I diabetes, and food allergies.

This work presents the modification and characterization of an electrochemical H_2O_2 sensor to measure physiological concentrations in the human gut. Different electrochemical modifications have been explored, including the addition of Nafion®, to mitigate the fouling effect, and carbon nanotubes to improve the electron transfer. Copper, ceria, platinum, and silver metals, are compared as catalyzers for the H_2O_2 reduction. Sensor performance was evaluated with cyclic voltammetry and amperometric measurements using a benchtop potentiostat, as well as a portable potentiostat, AD5941 front-end development kit (Analog Devices), to validate the feasibility for miniaturization into a potential smart capsule device. The results showed that, although copper coverings provide better sensitivity, platinum electrodes with a Nafion® coating was observed the better approach for sensing H_2O_2, in terms of simplicity, reproducibility and reliability for prolonged experiments. Changes in the pH produce negligible changes on the sensor performance. Additionally, a limit of detection of 25 μmol L^{-1} and a mean recovery of ca. 90% was observed when on the sensor was immersed in artificial intestinal fluid.

BI-Contributed On Demand-40 Electrochemical Activation of CNT-coated Carbon Fiber Microelectrodes for Serotonin Sensing*, **Jinjing Han**, S. Botasini, A. Chapin, R. Ghodssi,* University of Maryland, College Park

Serotonin (5-hydroxytryptamine, 5-HT) is a key neurotransmitter in the brain, contributing to the pathophysiology of mental health disorders, such as anxiety and depression. 5-HT measurement *in vivo* requires real-time measurement techniques with high sensitivity because of its low concentration. For decades, carbon fiber (CF) based electrochemical sensors have been the predominant detection method for 5-HT in biological samples due to their fast response time, wide linear response, and low cost. Therefore, further improvements towards high-sensitivity carbon fiber microelectrode (CFMEs) for electrochemical 5-HT detection are required for *in vivo* monitoring.

Here, we combine two surface modification methods to the CFME: 1) coating with Nafion/carbon nanotubes (CNTs) and 2) applying an electrochemical pretreatment. First, CNTs dispersed by Nafion in isopropanol (IPA) were dip-coated onto a bare CF (Nafion-CNT@CF). Then, electrochemical pretreatment was performed by immersing the coated CFME in phosphate-buffered saline (PBS) and applying two triangular waveforms sequentially: an oxidation waveform (0 V to +2.5 V) followed by a reduction waveform (0 V to -1.5 V) (Nafion-CNT/EC@CFs). The CNT coating dramatically increases the electrode specific area, which is further increased by electrochemical pretreatment via an electrochemical etching effect. Both surface coating and electrochemical pretreatment increase surface area and surface roughness to form additional binding sites, resulting in higher sensitivity to 5-HT.

Initially, the electrode performance was characterized in 10 µM of 5-HT in PBS using cyclic voltammetry (CV) at 1 V/s scan rate. A well-defined oxidation peak was observed at 0.45 V (Fig. S1) with oxidation peak currents (Ipa) of 0.32 µA and 1.25 µA for Nafion-CNT@CF and Nafion-CNT/EC@CF, respectively. No oxidation peak was detected for the bare CF electrode. The Nafion-CNT/EC@CF showed a **3.9-fold increase** in current response to 5-HT compared to the Nafion-CNT@CF. Further characterization of the Nafion-CNT/EC@CF was conducted at various concentrations between 0.1 – 1 µM (Fig. S2). The Nafion-CNT/EC@CF exhibited a linear range (up to 1 µM, $R^2=0.9744$) with a sensitivity, determined using the slope of the linear region, of 0.19 µA/µM. The limit of detection (LOD) is calculated to be 370 nM. The combination of an additive surface coating and subtractive electrochemical pretreatment synergically increased the surface area for 5–HT binding events. The surface modified CFMEs provide a sensitive and label-free method to directly detect 5-HT electrochemically in real time, enabling the potential for sub-micromolar detection of 5-HT in biological samples.

BI-Contributed On Demand-43 Grafting-to of Biomimetic Bottlebrush Polymer*, L. Navarro, D. French, T. Shah, **Stefan Zauscher***, Duke University

Specifically-adsorbed bottlebrush coatings are found in nature as brush-like glycoproteins that decorate biointerfaces and provide anti-fouling, lubrication, or wear-protection. While protein-bottlebrush hybrids are promising proteoglycan mimics, many challenges still exist to robustly produce such polymers. We briefly report on a novel modular approach we have developed to synthesize protein-brush hybrids by copper-catalyzed azide-alkyne cycloaddition. Furthermore, the use of such proteoglycan mimics is still limited because of the current lack of understanding of their adsorption behavior and surface conformation. Here we thus describe the adsorption behavior of PEG-based, biotinylated bottlebrushes with different backbone and bristle lengths to streptavidin model surfaces in PBS. We used QCM, LSPR, and AFM, to elucidate how bottlebrush dimensions impact their adsorption kinetics, surface conformation, mechanical properties, and anti-fouling properties. We found that the adsorption behavior is characterized by three kinetic regimes: (I) a transport-limited regime, (II) a pause, and (III) a penetration-limited regime. We also found that bristle length more dramatically affects brush properties than backbone length. Specifically, larger bottlebrush dimensions lead to reduced molar adsorption, retarded kinetics, weaker anti-fouling, and softer brush coatings. WE believe that our findings aid the rational design of biomimetic bottlebrush coatings for a broad range of biomedical applications.

BI-Contributed On Demand-46 Design and Synthesis of Multifunctional Nucleotide Analogue Delivery Vehicles to Combat Cancer*, Y. Yang, S. Deshpande, A. Chilkoti, **Stefan Zauscher**,* Duke University

The use of DNA as a polymeric building material transcends its function in biology and is exciting in bionanotechnology for applications ranging from biosensing, to diagnostics, and to targeted drug delivery. Our research is motivated by the complexity and low yield of syntheses of current aptamer-targeted nanoparticle drug carriers that are typically carried out by multi-step chemical conjugation of aptamer and drug to a carrier. Here, we demonstrate a highly efficient in situ enzymatic polymerization strategy that "grows" a polynucleotide drug segment and a self-assembly segment from an aptamer "initiator." Specifically, we exploit the ability of a template-independent DNA polymerase —terminal deoxynucleotidyl transferase (TdT)— to catalyze the polymerization of 2'-deoxyribonucleoside 5'-triphosphates (dNTP, monomer) from the 3'-hydroxyl group of an oligodeoxyribonucleotide (initiator). We found that the reaction kinetics follows a "living" chain-growth polycondensation mechanism and that like in "living" polymerizations, the molecular weight of the final product is determined by the starting molar ratio of monomer to initiator. Our synthesis approach can incorporate a wide range of unnatural dNTPs into the growing chain, such as, hydrophobic fluorescent dNTP and 5-fluoro-2'-deoxyuridine (FdUTP), a nucleotide analog of the anticancer drug 5-fluorouracil (5-FU). This "one-pot" enzymatic reaction approach offers a new, dramatically simplified and innovative route for the synthesis of nuclease-resistant, multifunctional block- copolymers which can self-assemble into size-optimized micellar structures for drug delivery applications.

BI-Contributed On Demand-52 Structure Determination of Surface Bound Proteins: Are We There Yet?*, **David Castner**,* University of Washington

Controlling how proteins are immobilized is essential for optimizing the performance of *in vitro* protein-binding devices. Comprehensive analysis of surface immobilized proteins provides the level of detail about the immobilization process and the structure of the immobilized biomolecules needed to develop and optimize these devices. In particular, surface analysis methods such as x-ray photoelectron spectroscopy (XPS), time-of-flight secondary ion mass spectrometry (ToF-SIMS), sum frequency generation (SFG) vibrational spectroscopy, surface plasmon resonance (SPR) biosensing and quartz crystal microbalance with dissipation (QCM-D), when combined with Monte Carlo (MC) and molecular dynamics (MD) computation methods, provide a powerful method for obtaining information about the attachment, type, orientation, conformation and spatial distribution of surface immobilized proteins. Although much progress has been made in characterizing surface bound proteins over the past 40 years, the ability to provide atomic level structural information is still lacking, especially for large proteins. In recent years the combination of new computational and experimental methods has been used to obtained detailed characterization of model peptides and small proteins. In particular, Protein G B1, an immunoglobulin (IgG) antibody-binding domain of Protein G, has proven to be an excellent small protein for developing and expanding our ability to characterize the structure of surface bound proteins. Using protein engineering methods to site selectively introduce cysteine into the Protein G B1 structure provides a method for controlling its orientation on well-defined surfaces. Multi-technique characterization coupled with biological reactivity measurements were used to show the effect of Protein G B1 orientation on IgG antibody binding. The challenge now is to extend this approach to larger and more complex proteins. Another challenge is developing computation methods that can predict the structure of surface bound proteins. Also, it is important to continue to advance our ability to characterize protein structure under biologically relevant conditions such the 3D structures found in aqueous based environments. Sum-frequency scattering (SFS) spectroscopy is one method well suited for these measurements.

BI-Contributed On Demand-55 Chemical Changes On, and Through, The Bacterial Envelope in *E. coli* Mutants Exhibiting Impaired Plasmid Transfer Identified Using Time-of-Flight Secondary Ion Mass Spectrometry*, **Kelly Dimovska Nilsson**,* University of Gothenburg, Sweden*; M. Palm,* University of Gothenburg, Sweden, Centre for Antibiotic Resistance Research, University of Gothenburg, Sweden*; J. Hood, J. Sheriff,* School of Engineering, Newcastle University, UK*; A. Farewell,* Department of Chemistry and Molecular Biology, University of Gothenburg, Sweden, Centre for Antibiotic Resistance Research, University of Gothenburg, Sweden*; J. Fletcher,* University of Gothenburg, Sweden

Antibiotic resistance causes 25 000 deaths every year. The rate of the spread and the threat that antibiotic resistance pose on a global scale makes this a field of great interest for research. Transfer of plasmids (mobile DNA) between bacterial cells through conjugation is one of the major contributors to the spread of antibiotic resistance. A larger understanding of the mechanisms behind this process and how to possibly hinder it could help to quench the development observed around the world. In this study, the changes in lipid composition in the cell membrane of three mutated E. coli strains were analysed using a J105 - *3D Chemical Imager*.

Using a J105 (Ionoptika Ltd, UK), an unconventional, time-of-flight secondary ion mass spectrometry (ToF-SIMS) instrument coupled to a 40 keV CO_2 gas cluster ion beam (GCIB) allowed analysis of the outer membrane of mutated *E. coli* previously identified as having impaired plasmid transfer capability, related to the spread of antibiotic resistance, and how the lipid composition changed in the membrane due to the mutations. The sub-set of mutants were selected as the mutations were expected to result in changes in the bacterial envelope composition, through the deletion of genes encoding for FabF, DapF and Lpp, where the surface sensitivity of ToF-SIMS can be most useful. Analysis of arrays of spotted bacteria allowed changes in the lipid composition of the bacteria to be elucidated using multivariate analysis and confirmed through imaging of individual ion signals.

Significant changes in chemical composition were observed, including a surprising loss of cyclopropanated fatty acids in the *fabF* mutant where FabF is associated with the elongation of FA(16:1) to FA(18:1) and not cyclopropane formation. The ability of the GCIB to generate increased higher mass signals from biological samples allowed intact lipid A (*m/z* 1796) to be detected on the bacteriaand, despite a 40 keV impact energy, depth profiled through the bacterial envelope along with other high mass ions including *m/z* 2428, attributed to ECA_{CYC}, that was only observed below the surface of the bacteria and was notably absent in the depth profile of the Lpp mutant.

The analysis provides new insights into the action of the specific pathways targeted in this study and paves the way for whole new avenues for the characterization of intact molecules within the bacterial envelope.

BI-Contributed On Demand-58 Novel Bio-Inspired Urinary Catheter Reduces Protein Deposition and Incidence of Catheter-Associated Urinary Tract Infections*, **Marissa Andersen**,* University of Notre Dame*; J. Fong,* University of Maine*; A. LaBella, A. Molesan,* University of Notre Dame*; C. Howell ,* University of Maine*; A. Flores-Mireles,* University of Notre Dame

Urinary catheterization is a common procedure in healthcare facilities and catheter placement predisposes patients to the development of catheter-associated urinary tract infections (CAUTI), the most common nosocomial infection. Their treatment has become a high priority due to the rise of uropathogens' antibiotic resistance. Efforts have focused on development of vaccines, immunotherapies, and antimicrobial coated-catheter materials; the latter having shown promise *in vitro*, however in clinical trials, they are unsuccessful or yield mixed results. In humans and mice, we have shown that in response to urinary catheterization fibrinogen (Fg), a host protein, is released, deposited and accumulated on catheters. This allows Fg to serve as a scaffold for microbial colonization leading to an increase in initial pathogen binding to catheter surfaces as shown in previous studies. Deposited Fg may also hinder the release or availability of antimicrobials on coated-catheters and may also prevent direct contact with pathogens. This phenomenon could partly explain why antimicrobial-coated catheters show antibacterial effects *in vitro* but not *in vivo*. Therefore, we hypothesized that reducing Fg deposition will prevent uropathogen colonization of the catheter, a critical step for establishing infection and thus reducing the establishment of CAUTI. Our approach utilized infusing silicone catheters with liquid silicone to create a slippery surface which prevents protein deposition. With this material we found a significant reduction in Fg and uropathogen colonization on these modified catheters *in vitro.* Additionally, this modification showed a decrease not only in 91.2% of deposited host proteins on the catheter but also the burden of a group of six uropathogens during CAUTI, which correlated with the reduction of Fg deposition *in vivo.* Together, our findings suggest that anti-protein fouling urinary catheters may provide an effective antibiotic-sparing therapy against CAUTI.

BI-Contributed On Demand-61 Deconvolution of 3D OrbiSIMS Biological Datasets *via* Comprehensive Molecular Formula Prediction*, A. Kotowska, M. Edney, **David Scurr**,* University of Nottingham, UK

Modern mass spectrometry (MS) techniques produce a wealth of complex data-sets with a significant bottleneck in their analysis, this is especially so with biological samples. Existing analytical software has been successfully developed in LC/GC-MS and FT-ICR MS, some of which combines a molecular formula prediction with visualization of MS data through plotting of double bond equivalence (DBE) versus carbon number[1] (where DBE relates elemental composition to unsaturation in a molecule). This is typically an unused method in SIMS data analysis owing to the highly fragmented nature of the secondary ions and relatively few molecular ions being available. Datasets such as those acquired from the 3D OrbiSIMS utilising the gas cluster ion beam and OrbiTrap^{TM} analysis modes provide high mass resolved spectra including many molecular secondary ions. As such these data-sets are amenable to this analytical approach. In this series of work molecular formula prediction and data visualization has been demonstrated to effectively deconvolute complex biological data-sets in a manner which is unachievable using established approaches to SIMS analysis, such as targeted compound searching and/or untargeted methods including multivariate data analysis (MVA).

In this work we have developed software for formula prediction and data visualization, successfully applying it to 3D OrbiSIMS data acquired from frozen hydrated human skin tissue, human serum samples and freeze dried cultured cells. In the 3D OrbiSIMS analysis of human skin samples this approach has enabled the discrimination of chemical species present within skin including fatty acids, lipids, N-acyl ethanolamines, sterols, ceramides, glycerides (mono, di and tri) and amino acids. The software also allows for the illustration of the respective depth profiles for each species identified which can be used to rationalise their identity through their presence or absence within specific physiological layers. The chemically filtered data-sets are available for subsequent analysis using techniques such as MVA. Analysis of human serum samples showed that proteins and lipids were easily distinguished and 1,477 lipid peaks were automatically assigned and classified in the serum with the selection of protein related secondary ions having the potential to act as a filtering stage during protein identification using 3D OrbiSIMS[2]. Furthermore, in the analysis of cultured cells, amino acids, fatty acids, lipids, metabolites and sample substrate can also be readily separated and identified using this approach.

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BI-Contributed On Demand-64 Immiscible Liquid-Coated Filters Resist Biofouling*, **Justin Hardcastle**, D. Regan, C. Fong,* University of Maine*; R. Shah, S. Hung, A. Cihanoglu, J. Schiffman,* University of Massachusetts Amherst*; C. Howell,* University of Maine

During the purification of water and air, biofouling is an ongoing issue that leads to flow decay, and current chemical and physical cleaning methods for fouled filters can lead to filter degradation over time. In addition to being porous throughout, commonly used filters such as polytetrafluoroethylene (PTFE) and polyvinylidene fluoride (PVDF) often have a textured surface that promotes the adhesion of bacteria and other contaminants. In this work, we present bio-inspired liquid-coated filters as a new approach to creating filters that resist fouling. Liquid-coated filters were created by immobilizing a water immiscible liquid on the surface of commercially available synthetic filters. For water filtration tests, 0.45 µm pore diameter PTFE and PVDF filters were coated with omniphobic perfluoropolyether liquids. We measured the continuity of the surface liquid layer by testing how easily a water droplet could begin to move the surface, as well as the anti-adhesion properties of the surface liquid layer through quantifying the speed of a droplet's movement at a static angle of inclination. The results indicate that the PTFE membranes sustained a more consistent functional liquid layer, with an approximately 75% lower sliding angle and 70% faster droplet movement at a fixed angle, than the PVDF. Dead-end pure water permeability (PWP) experiments conducted at an applied pressure of 1.5 bar indicated that liquid-coated PVDF membranes had a statistically equivalent PWP of 2827 ± 323 L/m^2-h-bar, for over 10 cycles of use. For aerosol filtration, we tested the efficiency in capturing and releasing aerosolized *Escherichia coli* using liquid-coated commercial PTFE and HEPA filters. We determined that bacteria trapped on the liquid-coated filters could be removed with increased efficiency compared to bare controls. The use of liquid-coated materials in water and air purification applications opens new doors for the creation of a biointerface that resists adhesion in dynamic environments.

BI-Contributed On Demand-67 A Graphene-Based Platform for Investigation of Protein Assembly by Infrared Nanospectroscopy*, **Xiao Zhao**, D. Li,* Lawrence Berkeley National Laboratory (LBNL), China*; Y. Lu,* Lawrence Berkeley National Laboratory (LBNL), Taiwan*; P. Ashby, M. Salmeron,* Lawrence Berkeley National Laboratory (LBNL)

The nanoscale structures and dynamical processes of proteins have been extensively studied by various imaging techniques such as electron microscopy and atomic force microscopy (AFM) in liquid. However, these imaging techniques can damage or perturbate the samples and do not provide chemically identification. This prevents a direct monitoring of structural and chemical evolution under physiological conditions. Herein, we demonstrate a new nondestructive platform that enables nanoscale Infrared (IR) spectroscopy for S-layer protein at graphene-aqueous solution interface by combining graphene liquid cell and Fourier Transform Infrared Nanospectroscopy (nano-FTIR). Single layer graphene separating the assembly solution and the tip minimize the sample damage and tip contamination. The protein structural evolution during and after assembling process is monitored by recording the amide I and II vibration bands, which provides unique and complimentary information to the AFM morphology in liquid. Our platform opens up broad opportunities for *operando* study of soft materials or nanostructures (enzyme, membrane protein, virus, and plastic material) in their realistic condition and under external stimuli.

BI-Contributed On Demand-70 Analysis of Intact Proteins in the 3d Orbisims*, **Anna Kotowska**, G. Trindade, P. Williams, J. Aylott,* University of Nottingham, UK*; A. Shard,* National Physical Laboratory (NPL), UK*; M. Alexander, D. Scurr,* University of Nottingham, UK

The identification of proteins at surfaces has applications in studying biosensors used in the biotechnological field and cell interactions with biomaterials [1][2]. Secondary ion mass spectrometry (SIMS) is a surface analysis technique with lateral resolution below 200 nm and has been applied for the characterisation of protein functionalized surfaces. However, intense protein fragmentation by the primary ion beam results in only limited information about protein identity, conformation or orientation by statistical analysis of single amino acid ion intensities. The use of large gas cluster ion beams (GCIB) as analysis beams has allowed for more information to be derived from peptide samples (up to 3kDa) in SIMS by detection of multi amino acid fragments [3]. However, these distinct ions have not previously been identified for proteins.

Here we use the 3D OrbiSIMS (HybridSIMS, IONTOF GmbH) [4], combining an argon GCIB primary ion beam and the Q Exactive^{TM}analyzer to identify proteins directly from a surface. In sixteen example proteins in a range of sizes from 6 kDa (insulin) to 272 kDa (fibronectin), up to 12-membered amino acid sequences were detected and assigned using the *de novo* sequencing approach. The multi amino acid fragments were assigned with confidence due to the high mass accuracy (<2 ppm) and the MS/MS capability of the instrument. This illustrates the potential to identify proteins adsorbed on the surface and utilise the 3D OrbiSIMS in characterising interactions of proteins with materials used in tissue engineering and medical devices.

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BI-Contributed On Demand-73 Cell Instructive Materials for Next Generation Medical Devices: Microtopography Opportunities*, **Morgan Alexander**,* The University of Nottingham, UK

The range of 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 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. [1,2,3] This approach is akin to engineering serendipitous discovery and will be exemplified using examples that have been taken from the lab all the way to the clinic.

The latest work combining from this bio-instructive materials area micro topography combined with bio-instructive polymer chemistries including the TopoChip[4,5], ChemoTopoChip [6] and the ArchiChips [unpublished] will be highlighted in this talk.

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Acknowledgements

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BI-Contributed On Demand-76 Physical Virology of SARS-CoV-2 Uptake and Adhesion*, S. Kumar,* University of Texas at Austin*; A. Paul,* University of Texas at Austin, Chalmers University of Technology, Sweden*; N. Nehra, D. Wang, A. Nisar, **Sapun H. Parekh**,* University of Texas at Austin

The SARS-CoV-2 novel coronavirus disease has caused a global pandemic disease that has spread globally to more than160 countries, disrupting global health and costing trillions in economic damage in the process.

SARS-CoV-2 infects host cells primarily by binding Angiotensin-Converting Enzyme 2 (ACE-2) surface receptor via its Spike (S) protein. Substantial efforts have gone into sequencing the virus and understanding its biochemistry, but remarkably little is known about the biophysics of the virus or its entry process into cells. The virus infection data reveal some interesting physical trends: 1) global data on SARS-CoV-2 indicates improved stability of the virus at lower temperatures, 2) there is a higher infectious risk for older people – with more fibrotic (stiffer) lungs, and 3) the particle exhibits very different lifetimes on different surfaces. From a physical perspective, SARS-CoV-2 is a ~ 100 nm polymer particle with a lipid envelope and protein shell, and its S protein binds to a cell receptor causing internalization. In this sense, it is no different than a typical polymer nanoparticle that biomaterial scientists have been working with for years. Here investigate the SARS-CoV-2 virus from a physical science perspective using viral mimic particles: S protein coated nanospheres and S protein containing pseudo-typed viruses. We report adhesion strengths for different surfaces and study viral uptake into lung airway cells as a function of different host temperatures and the stiffness of underlying “lung” tissue matrix. We find that physical variables affect uptake, and our results suggest viral infection is indeed elevated for stiffer lungs, similar to what is seen in the clinic. We also compare results from the nanosphere and pseudo-type virus systems and in an effort to highlight where our physical approach falls short and where it is appropriate. We hope this work not only provides a better understanding on how physical factors influence viral transmission and pathogenicity but also demonstrates the opportunities of taking a physical science to virology.

Biomaterial Interfaces Division

Room On Demand - Session BI-Invited On Demand

Biomaterial Interfaces Invited On Demand Session

BI-Invited On Demand-1 Ion-Assisted Plasma Polymerization: Surface Engineering of Biomimetic Interface*, Behnam Akhavan*, *M. Bilek,* The University of Sydney, Australia **INVITED**

Titanium-based alloys are promising materials for orthopedic prostheses due to their low toxicity, superb corrosion resistance, and favourable mechanical properties. The sub-optimal biocompatibility of bare metal surfaces, however, often leads to adverse foreign body responses, inflammation, or infection requiring additional medical interventions. The integration of metallic implantable devices with local host tissues can be strongly improved by a plasma polymerized (PP) coating functionalized with biomimetic molecules. The stability of the PP layer in body fluids is indispensable, and the coating must resist failure even when scratched. In this presentation, I talk about a novel approach for the fabrication of chemically and mechanically robust PP coatings on titanium surfaces. A custom-made plasma polymerization system consisting of a radio frequency (RF) electrode and a pulsed voltage source was utilized for PP deposition. The chemical and mechanical stability of the coatings in simulated body fluid (SBF) was examined by incubation of samples in Tyrode’s solution at 37 °C for durations of up to 2 months. As evidenced by both X-ray photoelectron spectroscopy (XPS) data and scanning electron microscopy (SEM) observations, the PP coating resisted failure, and no delamination, cracking, or buckling was observed after scratching and subsequent incubation in SBF solution. XPS results revealed that the excellent interface adhesion is linked to the formation of metallic carbide and carbonate bonds, induced by ion implantation, at early stages of film growth. Such atomic interfacial mixing also resulted in the formation of a continuous smooth film near the substrate as suggested by atomic force microscopy (AFM) and time of flight secondary ion mass spectroscopy (ToF-SIMS) data. I present results demonstrating that multifunctional protein layers, peptide molecules, or silver nanoparticles can be covalently immobilized on such interfaces for improved osteoblast activity and enhanced antimicrobial properties. I also describe our recent work on tuning the orientation and density of immobilized molecules on these PP coatings by tuning pH or applying external electric fields during the biomolecule immobilization.

BI-Invited On Demand-7 NanoSIMS Imaging of Cholesterol and Sphingolipids in Cell Membranes*, Mary Kraft,* University of Illinois at Urbana-Champaign **INVITED**

Regions with different protein and lipid compositions are present in the plasma membranes of mammalian cells. Correlations between the activities of specific membrane proteins and their distributions within the plasma membrane have been drawn from studies that combined functional assays with the selective imaging of the protein species of interest within the plasma membrane. Certain lipid species and cholesterol are also hypothesized to have non-random distributions within the plasma membrane that may be required for proper cell function. We tested this hypothesis by using high-resolution secondary ion mass spectrometry (SIMS) performed with a Cameca NanoSIMS to image isotope-labeled lipids and cholesterol within mammalian cell membranes with ≤100-nm-lateral resolution. First, we metabolically incorporated ^{15}N-sphingolipids and ^{18}O-cholesterol into the membranes of two mammalian cell lines. Next, we used a Cameca NanoSIMS 50 to image the component-specific isotopic (^{15}N and ^{18}O) and elemental (gold) enrichments in the plasma membrane with a lateral resolution of approximately 100 nm. Finally, we assessed co-localization between the cholesterol and sphingolipids with statistical methods.We found that sphingolipids are enriched within distinct regions within the plasma membrane, but the cholesterol distribution is relatively uniform. This work argues against the prevailing hypothesis that the plasma membranes of mammalian cells contain domains that are enriched with both cholesterol and sphingolipids.

BI-Invited On Demand-13 Materials inspired from Catch Bonds and other Biological Adhesion Strategies*, Sinan Keten,* Northwestern University **INVITED**

Biological materials excel at serving mechanical functions, which may be passive as in structural materials, or dynamic, as in cell motility and adhesion components. Impressive properties of biomaterials often come from novel designs of interfaces and adhesive mechanisms. In this talk, I’ll summarize our recent progress on modeling biological adhesion mechanisms at the molecular scale, using innovative coarse-grained simulation techniques. I’ll present new advances in interface design enabled by molecular and multi-scale simulations, and translation of developed ideas to nanocomposite design. I’ll talk about computational design of polymer grafted nanoparticle assemblies and how interfaces in these materials could take inspiration from bioadhesives to achieve superior stress transfer between nanoparticles. I’ll also discuss how examining basic allosteric principles of catch bonds in proteins could be reduced to simple mechanical models to create nanoparticle linkages with counterintuitive force-dependent kinetics.

BI-Invited On Demand-19 Contact Mechanics of Hydrogels*, Yuhang Hu,* Georgia Tech*; Y. Lai, D. He ,* Georgia Institute of Technology **INVITED**

Gel is composed of cross-linked polymer network and solvent molecules. Gels have broad application in many engineering fields such as drug delivery, tissue scaffold, soft robots and so on. Mechanical characterization of soft gels has been challenging. Recently there is a growing interest in using indentation techniques on gels because of the practical easiness. While relaxation indentation has been developed in characterizing the poroelastic properties of gels, dynamic indentation has been found to provide more accurate measurements in small scale, in which the gel is under oscillatory loading. In this study, we use the characteristic phase lag between the applied indentation displacement and the force on the indenter due to the energy dissipation from solvent flow in the gel to characterize the poroelasticity of gels. We will show that the phase lag degree is a function of two parameters, Poisson’s ratio and normalized angular frequency. The solutions are derived for several shapes of indenters. The maximum value of the phase lag over a spectrum of actuation frequencies can be used to characterize the Poisson’s ratio of the gel, and the characteristic frequency corresponding to the maximum phase lag can be used to characterize its diffusivity. Besides poroelastic properties of gels, we also use indentation technique to explore the adhesion properties of gels. We carry out the experiment on gels across a wide range of length scales and time scales, and use cohesive zone model to extrapolate the adhesion properties of gels.

BI-Invited On Demand-25 Understanding the Role of Protein Deposition Associated to Catheter-induced Inflammation in the Development of CAUTI*, M. Andersen,* University of Notre Dame*; J. Fong, C. Howell,* University of Maine*;* ***Ana Flores-Mireles,*** University of Notre Dame **INVITED**

Urinary catheterization is a common procedure in hospital setting and nursing homes. Even though, urinary catheters are used to safely empty the bladder, placement of the catheter predispose the patient to develop a catheter-associated urinary tract infection CAUTI. Currently, CAUTI are the most common healthcare-associated infection worldwide and often leads to leading to bloodstream infections with 30% mortality. CAUTIs are a major threat to public health since their treatment and control are becoming challenging due to the rise of antibiotic-resistant pathogens. Urinary catheterization allows a diverse number of pathogens to colonize the bladder, something that otherwise would not occur. Therefore is imperative to understand how urinary catheterization renders the bladder susceptible to an infection. Previously, we found that urinary catheterization elicits bladder inflammation and mechanically disrupts the host defenses, compromising the host for microbial colonization. Our recent findings in mice and humans have shown that fibrinogen (Fg) is released and accumulated in the bladder in order to heal the damaged tissue. Fg is also deposited on catheters, coating them and forming a platform for colonization by *E. faecalis*, *S. aureus*, *C. albicans*, *E. coli*, and *A. baumanni*. We found that Fg levels modulate outcome of the infection, in the absence of Fg, *E. faecalis* is unable to stick to the catheter and colonize the bladder. On the other hand, high Fg levels enhance enterococcal bladder and catheter colonization, suggesting protein deposition on urinary catheters is a key factor for microbial infection. Therefore, we developed bio-inspired liquid-infused catheters that reduce Fg deposition *in vitro*. We tested in our mouse model of CAUTI, finding that liquid-infused catheters not only reduced protein deposition but also prevented biofilm formation of previously mentioned pathogens. This finding provides a new alternative to prevent CAUTI that does not contribute to microbial drug resistance.

Biomaterials Plenary Session: Materials and Biology for the Future of Energy and the Environment
Room On Demand - Session BP-Invited On Demand

Biomaterials Plenary Invited On Demand Session

BP-Invited On Demand-1 Programmable Icosahedral Shell System for Virus Trapping*, **Hendrik Dietz,*** TU Munich, Germany **INVITED**

Broad spectrum antiviral platforms that can decrease or inhibit viral infection would alleviate many threats to global public health. Nonetheless, effective technologies of this kind are still not available. Here we describe a programmable icosahedral canvas for the self-assembly of icosahedral shells that have viral trapping and antiviral properties. Programmable triangular building blocks constructed from DNA assemble with high yield into various shell objects with user-defined geometries and apertures. We create shells with molecular masses ranging from 43 to 925 Megadaltons (8 to 180 subunits) and with internal cavity diameters ranging up to 280 nm. The shell interior can be functionalized with virus-specific moieties in a modular fashion. We demonstrate this virus-trap concept by engulfing hepatitis B virus (HBV) core particles and adeno-associated viruses (AAV). We show inhibition of HBV core interactions with surfaces in vitro and demonstrate neutralization of infectious AAV exposed to human cells.

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BP-Invited On Demand-7 Reaction Microenvironments Formed by Bioinspired All-Aqueous Phase Separation*, **Christine Keating,*** Penn State University **INVITED**

Biological cells are highly organized with numerous subcellular compartments, many of which lack membranous boundaries. We are developing simple experimental models for these membraneless organelles based on liquid-liquid phase separation. Phase coexistence is a common phenomenon in aqueous solutions of polyelectrolytes and other macromolecules. Solutes such as ions, small molecules, and biopolymers can become compartmentalized by partitioning between the phases. This generates microenvironments that can impact reaction locations, rates, and outcomes. For example, RNA can be accumulated within polymer-rich aqueous droplets, enhancing ribozyme reaction rates. Distinct physicochemical properties of adjacent phases within multiphase droplets can enable solute sorting, such as accumulating single-stranded versus double-stranded RNAs in different phases, and can impact binding thermodynamics. Bioinspired compartmentalization by aqueous phase coexistence is of interest for understanding biological cells, their prebiotic ancestors, and their artificial analogues, and more generally for bioreactors. For example, multiphase all-aqueous emulsion droplets enable pre-organization of local reaction microenvironments to control the structure and local composition of organic/inorganic composite materials during synthesis.

Chemical Analysis and Imaging at Interfaces Focus Topic
Room On Demand - Session CA-Contributed On Demand

Chemical Analysis and Imaging at Interfaces Contributed On Demand Session

CA-Contributed On Demand-1 Capturing Charge-Dynamics of Ionic-Liquid Electrolytes Within Energy Storage Devices With Operando X-Ray Photoelectron Spectroscopy*, E. Oz,* Bilkent University, Turkey*; M. Basaran,* Koc University, Turkey*; B. Ulgut,* Bilkent University, Turkey*; C. Kocabas,* Manchester University, UK*; A. Kocabas,* Koc University, Turkey*; **Sefik Suzer**,* Bilkent University, Turkey

Energy Supply and Storage Systems play pivotal role in current and future scientific and technological activities, and batteries are still on top of the list. However, batteries are slow, since they involve sluggish chemical reactions. Electrical-Double Layer Capacitors, or Super-Capacitors have recently been proposed as alternative, since they involve movement of ions only through liquid/solid interfaces.[1] Transport of the ions also controlls performance of these devices and need to be investigated during their operation. XPS is one of the most informative surface analyses techniques, which can deliver chemical as well as electrical properties of systems, when used in-Operando (o-XPS). Unfortunately, the technique requires Ultra-High-Vacuum environment, not very suitable for volatile liquids like water, but there are also several non-volatile liquids, like ionic liquids, which are also excellent electrolytes for battery and super-capacitor applications. Emergence of Ionic Liquids with several promising properties, including their low volatility, has rekindled the use of XPS.[2] Our recent efforts have also concentrated on ionic-liquids and their interfaces under **dc** and **ac** bias, and extended to monitoring electrochemical reactions, as well.[3-5] The common theme in our studies is the use of the bias dependent shifts in the positions of the core-levels as reflection of the electrical potentials, recorded in a non-invasive and chemically resolved fashion. We use both **the magnitude** and **the frequency** dependence of such potentials to extract pertinent information related to static, as well as dynamic chemical and/or electrochemical properties of the materials and their interfaces, configured as devices,[6-7] with particular emphases on the ionic liquids' certain chemical/physical parameters, like steric effects, ion size, diffusivity, etc.[9] Examples using ionic liquids, liquid poly-ethylene-glycol (PEG) and salts, as well as their mixtures, as electrolytes, will be presented and discussed.

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CA-Contributed On Demand-4 Operando Spatiotemporal Potential Mapping of Ionic Liquid Polarization in a Coplanar Electrochemical Device Using Xps and Sem Comparatively*, **Sefik Suzer,*** Bilkent University, Turkey*; E. Strelcov, A. Kolmakov,* National Institute of Standards and Technology (NIST)

Effects of the electrical potential developments along a co-planar capacitor, having an ionic liquid as the electrolyte, have been examined by a combination of two powerful analyses techniques, X-Ray Photoelectron Spectroscopy and Secondary Electron Microcopy for investigating the polarization dependent spatio-temporal response of the system, while imposing the device to external DC or AC (Square-Wave) biasing. The applied potential screening manifest as binding energy shifts using XPS and intensity variations using SEM. The magnitude of the developed electrical potential can be extracted under both DC ($t = \infty$) and AC (fast 1 kHz and slow 10 mHz) bias using both techniques to yield similar time-constants. This similarity is surprising, considering the differences in the underlying principles of the detected signals of the two techniques, but brings out the power of a synergistic combination of the two techniques with complementary capabilities, XPS with a higher chemical specificity but a lower spatial resolution, SEM with a higher spatial resolution and faster data accumulation speed.

CA-Contributed On Demand-7 Selecting a Water-lean Solvent for CO_2 Capture Using Liquid ToF-SIMS*, Jun Gao*, *Y. Zhang, J. Son, Z. Zhu, D. Heldebrant, R. Rousseau, X. Yu,* Pacific Northwest National Laboratory

Water-lean solvents are considered a promising technology for carbon dioxide (CO_2) capture. Such solvent molecules include but not limited to N-(2-ethoxyethyl)-3-morpholinopropan-1-amine (2-EEMPA), 3-methoxy-N-(pyridine-2-ylemthyl)propan-1-amine (MPMPA), and 1-((1,3-Dimethylimidazolidin-2-ylidene)amino)propan-2-ol (IPADM-2-BOL). To better apply these solvents for direct air capture of CO_2, it is necessary to understand the molecular structures, chemical compatibility with separation membranes, and CO_2 capture mechanisms. In this presentation, we will compare the three prominent water-lean solvents as CO_2 capture candidates.Non-CO_2 loaded and CO_2 loaded amine-based solvents were studied using static and *in situ* time-of-flight secondary ion mass spectrometry (ToF-SIMS). Static SIMS is used to assure peak identification.We investigate the water-lean solvents using mass spectral imaging, namely time-of-flight secondary ion mass spectrometry (ToF-SIMS).Static SIMS was used to acquire high mass resolution reference spectra and support peak identification.In situ liquid SIMS imaging was performed to study liquid structural changes and select the optimal CO_2 capture solvent using the system for analysis at the liquid vacuum interface (SALVI) microreactor. Characteristic peaks indicative of 2-EEMPA were observed using in situ liquid SIMS, for example m/z^- 73 $C_4H_9O^-$, 86 $C_4H_8NO^-$ in the negative mode and m/z^+ 29 $C_2H_5^+$ and 128 $C_7H_{14}NO^+$ in the positive mode. The pseudo-molecular peaks, m/z^- 215 $C_{11}H_{23}N_2O_2^-$ deprotonated 2-EEMPA in the negative mode and m/z^+ 217 $C_{11}H_{25}N_2O_2^-$ protonated-2-EEMPA in the positive mode, were also observed, showing the power of molecular detection of liquid ToF-SIMS. In addition, ion pair peaks were observed including m/z^+ 261, 305, 349, and 393 corresponding to EEMPA···nCO_2, n=1-3, respectively, in the positive mode and the product peak of m/z^- 61 CHO_3^- in the negative mode, all suggesting complex solvent structural changes as a result of CO_2 capture in the water-lean solvents. These new in situ observations, mass spectral analysis, and liquid structural simulation facilitate the selection of a suitable candidate in direct air capture for follow-on applications.

CA-Contributed On Demand-10 Algorithms for Automatic Analysis of Image Based Process Control and Its Implementation from Lab to Fab*, Julien Baderot,* *H. Ozdoba, D. Misra, N. Clement, S. Martinez, J. Foucher,* POLLEN METROLOGY, France

The need for automatic tools for the metrology of semiconductor structures is more and more pressing as processes become more challenging. In addition to these tools for metrology, it is important to be able to easily transfer the process knowledge from the laboratory to the production chain. Current solutions in the semiconductor industry, mainly propose manual tools and transition from Lab to Fab is tedious and clumsy which results in slow yield ramp-up.

During R&D stages, there is a wide variability in the shape and size of objects before achieving the maturity of the recipe. For this reason, we developed a unique metrology software platform that allows users to perform automatic analysis of complex images, coming from TEM or SEM microscopes. Automation during R&D cycles is becoming a reality thanks to state of the art machine learning and deep learning approaches to overcome current traditional algorithm limitations. This metrology platform provides tools that allow users to define their structures of interest and the associated measurements. Once the structures are defined, users can analyse their images automatically and access their measurements, even with the inherited variability of R&D.

The machine learning pipeline, we present two linked strategies. The first focuses on object detection. It requires the user to annotate a rectangular box around their objects. The shape and aspect are covering any type of semiconductors structures including fuzzy boundaries such as fins, slanted structures or pillars. For the second strategy, we propose an instance segmentation method to extract precise boundaries of the defined structures.

Then, for the implementation of the algorithms library, we propose different tools that enable the use of the algorithms in a fab environment. The first one is the API (Application Programming Interface) which allows the automatic analysis of images through the Manufacturing Execution System (MES). The API will provide a report for each analysis to feed Statistical Process Control (SPC) tools. Realtime demo of the software platform will be shown on several applications such as 3D Memory, Logic, AR/VR materials. Finally, key performance indicators will be presented and discussed.

CA-Contributed On Demand-13 Factors Influencing Surface Carbon Contamination in Ambient-Pressure X-Ray Photoelectron Spectroscopy Experiments*, Nicolo' Comini,* *Z. Novotny, J. Diulus,* University of Zurich, Switzerland*; T. Huthwelker,* Paul Scherrer Institut, Switzerland*; J. Osterwalder,* University of Zurich, Switzerland

Carbon contamination is a notorious issue that has an enormous influence on surface science experiments, especially in near-atmospheric conditions.While it is often mentioned in publications when affecting the experimental results, its causes are rarely analyzed in detail. Usingambient-pressure X-ray photoelectron spectroscopy,we analyzed the build-up of carbon species(both inorganic and hydrocarbons) on a clean, well-orderedsurface using large-scale (50×10 mm^2) rutile TiO_2(110) single crystals when exposed to water vapor and liquid water[1].

Various factors and environmental conditions, such as beam illumination, residual gas pressure composition, as well as interaction with liquid water, are shown to play a role in the build-up of carbon. It became evident that beam-induced effects locally increase the amount of carbon in the irradiated area. At the same time, starting conditions independent of the light irradiation determine the initial overall contamination level. The introduction of molecular oxygen in the order of 10 mbar can be utilized for fast surface cleaning during X-ray illumination. The surface carbon can be completely removed when the oxygen partial pressure is comparable to the partial pressure of water. Our results support the hypothesis that progressive removal of carbon species from the chamber walls by competitive adsorption of water molecules following repeated exposure of the experimental chamber to water vapor.We believe that these findings will be useful for future studies of liquid-solid interfaces using tender X-rays, where carbon contamination plays a significant role.

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CA-Contributed On Demand-16 Effects of Electrolytes on the Oxidation and Corrosion of Iron Interfaces Using PM-IRRAS*, Kathryn Perrine,* Michigan Technological University

Corrosion is an expensive problem for materials degradation that involves reactions that occur at the gas/solid and liquid/solid interfaces. These complex reactions involve surface chemical and physical changes including ion adsorption, charge transfer, redox reactions, pitting, and film growth. Iron surfaces are the classic material that corrodes, in both gases and liquids, through spontaneous redox reactions. At the liquid/solid interface, iron is oxidized at the anode with oxygen and water reduced at the cathode. Complexity arises from the presence of ions, which catalyze the surface reaction, and gas adsorption, transforming the metal surface into oxides and minerals. Chloride ions initiate the corrosion by breaking down the oxide layer and pitting the surface. Inorganic scale is grown as a result of buildup on the surface. However, the role of cations is unknown in this surface reaction. Understanding these fundamental processes are critical to addressing materials infrastructure degradation, mineral cycling, and other natural processes on Earth and other planets. Minerals, soils, and atmospheric dust are composed of iron, whose surfaces undergo electrochemical and catalytic reactions in the water and mineral cycles. Our research is presented to investigate iron surface oxidation and corrosion at the gas/liquid/solid interface using a surface catalysis approach.

We developed a new method that uses polarized modulated infrared reflection absorption spectroscopy (PM-IRRAS) with a liquid meniscus on a surface to measure the initial stages of surface oxidation and corrosion at the air/liquid/solid interface. This technique allows for observing the reaction of gradual atmospheric O_2 and CO_2 adsorption to the electrolyte/iron interface. In this presentation, the role of cations in chloride electrolytes was investigated on the oxidation and corrosion of iron interfaces. Iron surfaces were exposed to mono- and di-cation chloride electrolytes. We show how our PM-IRRAS method is used to observe the kinetics of oxidation and resulting formation of minerals at the air/electrolyte/iron interface. These results are corroborated with *ex situ* XPS and ATR-FTIR spectroscopy to measure the chemical changes of the interface. The physical changes of the surfaces were measured using *in situ* liquid AFM measurements during corrosion at the electrolyte/iron interface and after oxidation from O_2 and CO_2 at the air/iron interface. The findings of our studies suggest that cation partitioning at the air/electrolyte/iron interface catalyze and influence the mineral film formation in contrast to iron in the electrolyte, with no gradual adsorption of O_2 and CO_2. These results demonstrate how our PM-IRRAS method can be used to track other intermediate stages at gas/solid and liquid/solid interfaces for understanding electrochemical, catalytic, and environmental processes.

CA-Contributed On Demand-19 *in situ* XPS for Catalysis; Up to and Above One Bar*, Christopher Goodwin,* Stockholm University, Sweden*; P. Loemker,* Deutsches Elektronen-Synchrotron, Germany*; M. Shipilin, D. Degerman, P. Amann, A. Nilsson,* Stockholm University, Sweden

The pressure gap is a well-known obstacle in the development of instrumentation and catalysis. We have developed a new instrument that can perform truly high-pressure X-ray photoelectron spectroscopy (XPS) measurements, up to and over 1 bar. With the new pressure regime opened, many reactions now become possible to study. We will present several ongoing projects, including CO oxidation, methanol synthesis, Haber-Bosch process, and Fischer–Tropsch catalysis. With the higher-pressure ranges that can now be reached, direct measurements of industrial systems can yield new levels of understanding at the atomic scale.

CA-Contributed On Demand-22 Electrically Detected Magnetic Resonance & Near-Zero Field Magnetoresistance in ^{28}Si/^{28}SiO$_2$*, Elias Frantz,* Penn State University*; D. Michalak,* Intel Corp.*; N. Harmon,* University of Evansville*; E. Henry,* Intel Corp.*; M. Flatte,* University of Iowa*; S. King, J. Clarke,* Intel Corp.*; P. Lenahan,* Penn State University

We report low- and high-frequency electrically detected magnetic resonance (EDMR) and near-zero field magnetoresistance (NZFMR) measurements observed through spin-dependent trap-assisted-tunneling on unpassivated Si/SiO_2 metal-insulator-semiconductor (MIS) capacitors containing silicon of natural isotopic abundance and silicon depleted of ^{29}Si. This study explores the effects that electron-nuclear hyperfine interactions from nearby magnetic nuclei have on both the EDMR and NZFMR spectra. Although our measurements involve monitoring the spin-dependence of the trap-assisted-tunneling current responsible for leakage across the oxide, the high-frequency EDMR spectra resemble that of a combination of P_{b0} and P_{b1} silicon dangling bonds sites at the Si/SiO_2 interface. Additionally, we observed a half-field response in our low-frequency EDMR spectrum with the removal of ^{29}Si nuclei, indicating a small spin-spin separation distance. Capacitance versus voltage measurements also indicate a high interface trap density. These results suggest that the EDMR response is dominated by interface traps. We also observe a substantial narrowing of the NZFMR response with the removal of ^{29}Si nuclei. Since superhyperfine interactions between silicon dangling bonds at the Si/SiO_2 interface should be a full order of magnitude stronger than such interactions involving silicon dangling bonds defects (E’ center) within the oxide. Thus, the NZFMR results also strongly suggest a response dominated by Si/SiO_2 interface traps. These results collectively suggest very strongly that the leakage currents which we observe involve tunneling from Si/SiO_2 P_b dangling bonds to defects within the oxide, presumably oxide dangling bonds, that is E’ centers. Our results offer fundamental insight into technologically important phenomena involving oxide leakage currents in metal-oxide-semiconductor devices such as stress induced leakage currents and time dependent dielectric breakdown.

Acknowledgements

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This work was also partially supported by the Intel Global Supply Chain internship program.

CA-Contributed On Demand-25 Atomic-Scale Dynamics of Epitaxial Oxide Growth During Cu Oxidation Revealed by in Situ ETEM and DFT*, Meng Li,* *M. Curnan, S. House, W. Saidi, J. Yang,* University of Pittsburgh

The initial oxidation processes of metals and alloys are essential for a fundamental understanding of oxidation and play key roles in corrosion prediction, catalyst design, and oxide control. Instead of uniform oxide films, 3D oxide islands are observed in many metals and alloys during initial oxidation. However, the mechanisms for 3D oxide growth are still not clear, especially at the atomic scale. Using correlated in situ environmental transmission electron microscopy (ETEM), statistically-validated quantitative analysis, and density functional theory calculations, we show epitaxial Cu2O nano-island growth on Cu is layer-by-layer along Cu_2O(110) planes, regardless of substrate orientation, contradicting classical models that predict multi-layer growth parallel to substrate surfaces. The mechanism for this unusual layer-by-layer growth is elucidated using correlated density functional theory calculations and statistically validated quantitative analysis. These results shed new light on the epitaxial oxide growth mechanism and provide a deeper understanding of the dynamic processes involved in initial oxidation, which will ultimately help to precisely predict, design, and control nanostructured oxide growth.

Reference

M. Li, M. T. Curnan, M. A. Gresh-Sill, S. D. House, W. A. Saidi, J. C. Yang, Unusual layer-by-layer growth of epitaxial oxide islands during Cu oxidation. *Nat. Commun.***12**, 2781 (2021).

Acknowledgment

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CA-Contributed On Demand-28 Observing Plasma Assisted Processes *in situ* using SEM*, Andrei Kolmakov,* NIST

Multiple processes related to semiconductor microfabrication, aerospace industries, environmental remediation, and biomedical technology rely on plasma processing. Therefore, there exists a great need for *in situ* nanoscale imaging of surfaces under the plasma environment. This, however, is a challenging task for commonly used electron beam or scanning probe-based microscopies due to pressure gaps, signal interferences, strong spatial potential gradients and, etc [1]. Recently, we proposed a microflow discharge reactor equipped with a few-10s nm-thick SiN membrane as a tool to image surfaces with near-field scanning-probe-based microwave microscope immediately (a few seconds) after plasma processing with a sub-100 nm spatial resolution [2]. These SiN membranes are also largely transparent to a few keV electrons and isolate high vacuum SEM column from plasma environment around the sample, and thus enables real-time SEM imaging of a surface of interest under plasma conditions. In this communication, using CVD graphene as a model system, we report on true operando SEM imaging of the plasma-assisted etching process. In particular, signal strength, frame rate, spatial resolution, probing depth, and beam-induced effects were evaluated. We observe that graphene degrades significantly after a few seconds of ca. 200 mW oxygen plasma treatment. Under optimal conditions, a spatial resolution below 10 nm and a frame rate on the order of 1 Hz can be achieved. We also found that the contrast formation in SEM is due to the local difference in the electron emission yields of the sample and the supporting SiN membrane and it can be affected by the presence of static charges in the SiN membrane. The plasma etching of the graphene often results in the formation of highly conductive filamentary structures - a phenomenon that requires further studies.

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CA-Contributed On Demand-31 Graphene Encapsulation Platform for Multi-Technique Spectromicroscopy of Biological Cells and Hydrated Objects*, C. Arble,* NIST-Gaithersburg*; H. Guo,* Southeast University, Nanjing, China*; A. Matruglio,* University College London, UK*; L. Vaccari,* Elettra-Sincrotrone Trieste, Italy*;* ***Andrei Kolmakov,*** NIST-Gaithersburg

Label-free methods of spectroscopy and microscopy of live cells offer the capability to examine the cellular functions and structure in-vivo thus providing valuable insight into biomolecular components of cells [1]. However, live cells require aqueous media to be in equilibrium with interstitial fluid to survive. This requirement is inherently incompatible with the vacuum-based analytical techniques that use soft x-rays and electrons and impedes electron or soft x-ray imaging and spectroscopic studies under physiological conditions. The recent development of ultrathin molecularly impermeable X-ray (electron) transparent membranes, i.e. graphene, makes it possible to isolate the hydrated sample environment from UHV conditions and thus apply powerful spectromicroscopy tools that previously have been only used with vacuum compatible samples [2]. This approach can now be extended to (bio-) medical samples and interfaces.

Herein we report the design and fabrication of graphene encapsulated liquid cell platform for in-vivo studies of hydrated biological samples with a photon (Vis, IR, and soft X-rays) and electron-based spectromicroscopies that operate both under ambient condition and high vacuum environment.

The platform consists of an array of microfabricated 50 nm thick SiN windows allowing for combinatorial batch samples analysis both in transmission and reflection signal acquisition geometry. The samples are immobilized on top of the SiN windows and wet-encapsulated conformally with graphene. The encapsulation allows the sample to be isolated from the ambient and yet have its nutrition media preserved and sufficient to be studied with conventional analytical techniques [3]. This approach minimizes the volume of liquid retained along the optical axis, reducing the parasitic absorption and scattering while still providing cells with nutrients via peripheral cites [4]. Combining the sample immobilization with an onboard biocompatible hydrogel feeding media allows for extended cellular lifetimes during the measurement. Preliminary results on the viability of graphene encapsulation for biological samples were conducted with fluorescence optical, fluorescence, SEM, and synchrotron radiation bases XRF and FTIR spectromicroscopies.

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CA-Contributed On Demand-34 Ultrathin Free-Standing Oxide Membranes for Environmental Spectroscopic Study of Solid-Gas and Solid-Liquid Interface*, X. Zhao,* Lawrence Berkeley National Laboratory (LBNL), China*; Y. Lu,* Lawrence Berkeley National Laboratory (LBNL), Taiwan*; C. Carlos,* Lawrence Berkeley National Laboratory (LBNL), Spain*; M. van Spronsen,* Diamond Light Source, UK, Netherlands*; **Miquel Salmeron,*** Lawrence Berkeley National Laboratory (LBNL)

Many surface-sensitive techniques have been improved recently to narrow the gap between measuring environmental conditions from vacuum to practical gas and liquid environments. To extend the pressure range and to enable measurements of the liquid phase, thin film membranes acting as windows in environmental cells have been fabricated. Herein, we present a new generation of ultrathin (2-3nm) free-standing oxide membranes made with oxide films (Al_2O_3, TiO_2, etc.). The films, synthesized using Plasma Enhanced Atomic Layer Deposition (PE-ALD), are mechanically robust and transparent to electrons and photons. Their applicability for various environmental spectroscopies, such as X-ray Photoelectron Spectroscopy (XPS, 1bar) and Fourier Transform Infrared Nanospectroscopy (nano-FTIR, solid-liquid interface) is demonstrated. The remarkable properties of such ultra-thin oxide membranes open up broad opportunities for atomic/molecular level studies of interfacial phenomena (corrosion, catalysis, electrochemical reactions, energy storage, geochemistry, and biology) in a broad range of environmental conditions.

Chemical Analysis and Imaging at Interfaces Focus Topic Room On Demand - Session CA-Invited On Demand

Chemical Analysis and Imaging at Interfaces Invited On Demand Session

CA-Invited On Demand-7 Measuring the Depth Profiles of Surfactants, Ions, and Solvent at the Angstrom Scale*, X. Zhao,* University of Wisconsin - Madison*; G. Andersson,* Flinders University, Australia*; **Gilbert Nathanson,*** University of Wisconsin - Madison **INVITED**

We use neutral impact ion scattering spectroscspy (NICISS) to measure the depth profiles of ionic surfactants, their counterions and co-ions, and solvent molecules in liquid glycerol. The experiments yield an Angstrom-scale picture of how these species populate the interfacial region. The chosen surfactants are tetrahexylammonium bromide and sodium dodecyl sulfate in the absence and presence of additional sodium bromide. NICISS determines the depth profiles of the elements C, O, Na, S, and Br through the loss in energy of He^+ ions that travel into and out of the liquid, which is then converted into depth. In the absence of NaBr, we find that THA^+ and its Br^- counterion segregate together because of charge attraction, forming a narrow double layer that is 10 Å wide and 150 times more concentrated than in the bulk.With the addition of NaBr, THA^+ is "salted out" to the surface, increasing the interfacial THA^+ and Br^- concentration and spreading the ions over a ~30 Å depth. Added NaBr similarly increases the interfacial concentration of DS^- ions and broadens their positions. However, the dissolved Br^- ions are strongly repelled from surface DS^- because of charge repulsion. These different interfacial Br^- propensities correlate with previously measured gas-liquid reactivities: gaseous Cl_2 readily reacts with Br^- ions in the presence of THA^+ but drops 70-fold in the presence of DS^-, demonstrating that surfactant headgroup charge controls the reactivity of Br^- ions through changes in its depth profile.

CA-Invited On Demand-13 In-Situ/Operando Soft X-Ray Spectroscopy Characterization of Chemical Interfaces*, Y. Liu, X. Feng,* Lawrence Berkeley National Laboratory (LBNL)*; **Jinghua Guo,*** Lawrence Berkeley National Laboratory **INVITED**

The energy materials and devices have been largely limited in a framework of thermodynamic and kinetic concepts or atomic and nanoscale. Soft x-ray spectroscopy characterization offers unique characterization in many important energy materials of energy conversion, energy storage and catalysis in regards to the functionality, complexity of material architecture, chemistry and interactions among constituents within.

It has been found that the microstructure and composition of materials as well as the microstructure have a great influence on performances of energy conversion and energy storage materials, chemical and catalytic processes. However, it is challenging to reveal the real mechanism of the chemical processes. In-situ/operando x-ray spectra characterization technique offers an opportunity to uncover the phase conversion, chemical speciation at the solid/gas and solid/liquid interfaces in real time.

I will give some basics on in situ/operando soft x-ray spectroscopy characterization of interfacial phenomena in energy materials and devices, and how to use the powerful in-situ/operando characterization techniques, e.g. soft x-ray absorption spectroscopy (XAS) and resonant inelastic soft x-ray scattering (RIXS) to investigate the real electrochemical mechanism during the operation. A number of electrochemical liquid cells will be presented with success in revealing the catalytic and electrochemical reaction at real time.

CA-Invited On Demand-19 Direct-Write Electron Beam Processing of Topologically Complex Functional Nanomaterials using Thermo-Electrically Energized Multiphase Precursor Jets*, **Andrei Fedorov,*** Georgia Institute of Technology **INVITED**

Focused Electron Beam Induced Processing (FEBIP) is a powerful method for atom-by-atom fabrication of topologically complex nanostructures from a variety of materials. It provides a complete processing environment for emerging electronic and quantum devices based on 2D materials.[1] Energized micro/nano-jets of thermally or electro-kinetically energized precursors in both gas [2-4] and liquid [5] phase provide unique capabilities for localized delivery of precursor molecules to the substrate, thus establishing locally controlled deposition/etching site for FEBIP. This enhances the growth rate and purity by selectively tuning of precursor and contaminant sticking and surface diffusion coefficients as well as adsorption/desorption activation energies.[6] Expanding on gas-phase jet delivery of precursors, we recently demonstrated a new approach to FEBIP using liquid phase precursors delivered via a nanoelectrospray jetting process into a vacuum environment.[5] This enabled (1) dramatically increasing the growth rate of deposition/etching, (2) enabling deposition of composite materials and alloys with tailored electromechanical properties, and (3) fabrication of new, truly 3D topologies of nanostructures that are fundamentally out of reach of current gas-phase FEBID techniques. These unique new capabilities of NESA-FEBIP are matched by the complexity of the underlying physics and chemistry of ion transport and electrochemical reaction interactions, which need to be understood on the most fundamental level in order to take full advantage of and further develop new FEBIP modes and applications to emerging electronic and quantum devices based on 2D materials. I will highlight development and demonstration of a complete set of processing capabilities using FEBIP to fabricate devices from monolayer graphene, including high resolution, high speed etching [4], dynamic patterning and n-p-n junction formation [7,8], low resistance, Ohmic contact at the metal-graphene junctions [9], and "direct-write" reduction of graphene oxide, forming high electronic mobility conductive line patterns on the substrate. [10]

DOE BES Grant Support (DE-SC0010729) in acknowledged.

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CA-Invited On Demand-25 From Bulk to Constriction: Scaling Analysis of Ionic Transport Through Nanopores and Channels*, **Michael Zwolak**,* NIST*; S. Sahu,* University of Colorado at Boulder **INVITED**

Single pores through 2D materials, such as graphene and MoS_2, provide new opportunities for biochemical analysis and probing fundamental transport mechanisms of ions and molecules through confined environments [1]. For these "atomically thin" membranes, ion transport depends on dynamics both inside and outside the geometric volume of the pore due to several commensurate length scales, such as the effective membrane thickness, radii of the first and the second hydration layers, pore radius, and Debye length. We will demonstrate that a novel scaling analysis [2] and associated golden aspect ratio [3] enable all-atom molecular dynamics and other simulations to capture the transition between pore- and access-dominated ionic conductance as the pore radius increases beyond the effective membrane thickness (around 1 nm). In the pore-dominated regime, the physics of ion transport subdivides into mechanisms controlled by the free-energy landscape and diffusion. The latter again depends strongly on the flow of ions from bulk to the pore, just as in the access-dominated regime but now due to diffusive limitations and giving rise to sub-ohmic transport. A small strain applied to the 2D membrane can tune transport between these two mechanisms by modulating the balance of dehydration and electrostatic interactions via picometer changes in atomic positions and giving rise to optimal transport (and selectivity) regimes [4]. Overall, these concepts tie transport in nanoscale synthetic pores to transport in biological ion channels, as well as provide several tools for the rigorous simulation and modeling of biological and synthetic pores alike.

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Spectroscopic Ellipsometry Focus Topic
Room On Demand - Session EL-Contributed On Demand
Spectroscopic Ellipsometry Contributed On Demand Session

EL-Contributed On Demand-1 One-Pot Microwaved Synthesized Luminescent Carbon Quantum Dots From Various Citrus Fruit*, T. Gunawansa, **Sangram Pradhan**, M. Bahoura,* Norfolk State University

Green synthesized carbon quantum dots have been competitive alternatives to conventional heavily precursor dependent quantum dots due to their high biocompatibility, enhanced luminescent properties, simplicity, less toxicity, and repeatability all while being immensely cost-effective. Additionally, quantum dots are time-consuming to fabricate through standard wet chemical route. However, the utilization of a one-pot microwave allowed for the creation of more amount of size dependent luminescent carbon dots in short span by varying the cook time and fine controlled temperature. We have successfully synthesized carbon quantum dots from a variety of citrus fruits by fine-tuning the time, temperature, and pressure of the microwave. Furthermore, this comparative study highlighted the effects of the diverse fruit juices. After synthesis, the carbon quantum dots were characterized by transmission electron microscopy to determine nanostructure, Fourier transform infrared spectroscopy to analyze chemical bonding, ultraviolet-visible spectrophotometry, and photoluminescent spectrophotometry to evaluate absorption spectra and, emission/quantum yield of the materials respectively. These green synthesized one-pot microwaved carbon quantum dots have ample potential in enhancing optoelectronic, biosensing, and bioimaging applications.

EL-Contributed On Demand-4 Sub-Surface Imaging of Atomically-Thin Semiconductors Beneath Dielectrics Based on Optical Standing Wave Using Photoelectron Emission Microscopy With Deep-Ultraviolet Photoexcitation*, **Taisuke Ohta**, M. Berg,* Sandia National Laboratories*; F. Liu,* Los Alamos National Laboratory*; S. Smith, G. Copeland, C. Chan,* Sandia National Laboratories*; A. Mohite,* Rice University*; T. Beechem,* Sandia National Laboratories

Deep ultraviolet light sources provide new (and renewed) perspectives to photoemission experiments. In this talk, we will present an unconventional imaging approach using photoelectron emission microscopy to visualize two-dimensional materials sandwiched between amorphous thin-film dielectrics. Non-destructive imaging of fabricated nano-structures or nano-materials covered by dielectrics is highly sought after for diagnostics of optoelectronics devices. Exploiting the optical standing wave formation in the dielectrics cavity, we show imaging of atomically-thin MoS2 flakes buried beneath HfO2 overlayers up to 120 nm in thickness. The presence of MoS2 flakes modifies the optical response of the dielectric stack locally. Accordingly, the cavity resonance condition varies between the sample locations over buried MoS2 and surrounding areas, resulting in image contrast with submicron lateral resolution. This sub-surface sensitivity underscores the role of optical effects in photoelectron imaging with low-energy photons. Utilizing the optical effects and the overarching photoexcitation wavelengths in photoemission experiments presents possibilities to expand the materials and the phenomena of interests that can be pursued.

This work was supported by the Sandia LDRD and the Center for Integrated Nanotechnologies user program, an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science (DE-AC04-94AL85000). 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.

EL-Contributed On Demand-7 A Comparison of Mueller Matrix Spectroscopic Ellipsometry Based Scatterometry With Cd-Small Angle X-Ray Scattering for Measurement of Feature Size, Shape and Dimension for Nanowire Fet Test Structures*, **Alain Diebold**, M. Korde,* SUNY Polytechnic Institute*; R. Kline ,* National Institue of Standards and Technology*; D. Sunday,* National Institute of Standards and Technology (NIST)*; N. Keller, A. Antonelli,* ONTO Innovation

The first volume manufacturing of field effect transistors (FETs) based on vertically stacked, horizontal nanosheets and nanowires is expected by early 2021.Although leading edge manufacturing is now possible, routine non-destructive measurement of feature shape and dimension remains a significant and unmet challenge.In this presentation, we compare the measurement capability of Mueller Matrix Spectroscopic Ellipsometry based Scatterometry (MMSE-Scatterometry)[1] with synchrotron based CD-Small Angle X-ray scattering (CDSAXS)[2] for measurement of Feature Size, Shape and Dimension for Nanowire FET Test Structure (NWTS).[1] The NWTS is composed of a periodic array of contact hole structures etched into $Si_{(1-x)}Ge_x/Si/\ Si_{(1-x)}Ge_x/Si/Si_{(1-x)}Ge_x/Si$ multilayers. The measurement challenge is determination of the amount of selective etching of the subsurface $Si_{(1-x)}Ge_x$ layers. This is also known as the cavity etch. Our research shows that MMSE-scatterometry provides a rapid means of determining the average amount of etch and is sensitive to anisotropic changes in the contact hole.Our initial results show that CDSAXS may be sensitive to differences in the amount of etch of the individual $Si_{(1-x)}Ge_x$ layers.

49. Non-destructive characterization of nanoscale sub-surface features during selective etching of multi-layered Nanowire Test Structures using Mueller Matrix Spectroscopic Ellipsometry based scatterometry, M. Korde, S. Kal, C. Alix, N. Keller, G.A. Antonelli, A. Mosden, A.C. Diebold, J. Vac. Sci. Technol. B, 38, (2020), 024007.
50. Characterization of nanoscale sub-surface features during selective etching of multi-layered Nanowire Test Structures using Critical Dimension – Small Angle X-Ray Scattering, M. Korde, S. Kal, C. Alix, , A. Mosden, R.J. Kline, D. Sunday, and A.C. Diebold in preparation.

EL-Contributed On Demand-10 Optical Constants of GaSbBi as a Function of Bi Content and Temperature*, **John H. McElearney, K. Grossklaus, S. Lenney, M. Stevens, T. Vandervelde,* Tufts University

III-V-Bi semiconductor alloys, such as GaSb$_{1-x}$Bi$_x$, have garnered increased interest in recent years for their potential use in infrared optoelectronics. The Bi impurity state interacts with the host valence band edge to significantly reduce the film's bandgap [1]. In the case of GaSb$_{1-x}$Bi$_x$, reductions of up to 35 meV/% Bi have been reported for dilute concentrations [2]. Previous work also predicts a reduced temperature dependence of the bandgap [3,4], as well as suppressed Auger recombination with increasing Bi fraction [5]. As such, GaSbBi is a prime candidate for use in mid- to far-infrared devices, such as thermophotovoltaics, multi-junction solar cells, or IR photodetectors. To properly design these devices, however, requires a precise understanding of how the presence of Bi affects the material's optical properties.

In this work, we examine the optical constants of GaSbBi as functions of wavelength, Bi fraction and temperature by variable angle spectroscopic ellipsometry (VASE). Specifically, we determine the absorbance band edge energy, E_g, the refractive index, n, and the extinction coefficient, k, as functions of wavelength and Bi fraction for temperatures ranging from 80^o to 295^o -K. Optical data was collected using a J.A. Woolam VASE over a wavelength range of 300 nm to 3.2 µm. Samples were grown via molecular beam epitaxy (MBE) in a Veeco GenXPLOR system. Film composition was measured by x-ray diffraction and confirmed with bandgap measurements [5]. Surface morphology was examined via differential interference optical and atomic force microscopy. The results of this work will be crucial for accurate modeling of efficient mid- to long-infrared optoelectronic devices.

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EL-Contributed On Demand-13 A Machine Learning Approach to Thickness Prediction from in Situ Spectroscopic Ellipsometry Data for Atomic Layer Deposition Processes, ***S. Novia Berriel***, University of Central Florida*; A. Arunachalam,* University of Texas at Dallas*; C. Feit, U. Kumar, S. Seal,* University of Central Florida*; K. Basu,* University of Texas at Dallas*; P. Banerjee,* University of Central Florida

Spectroscopic ellipsometry (SE) is a powerful technique that can be used in situ for the purpose of monitoring atomic layer deposition (ALD) processes. Traditionally, raw data representing the change in polarization is captured and then fit to a physics-based model via software provided by the manufacturers of the SE equipment. The model allows for the determination of optical constants (n, k) and thickness of the film. We propose an alternate approach that makes use of a machine learning (ML) algorithm trained on existing optical models. It is then possible for the algorithm to directly extract thickness without the need for optical modeling thus, reducing data requirements and computational overhead costs.

We have trained multiple ML algorithms using optically modeled in situ ZnO ALD SE to predict thickness of a given set of polarization data (i.e., Y and D) from a ZnO film. The in situ data was obtained on a J.A. Woollam® M2000 ellipsometer attached to a FIJI Gen2 VEECO® ALD system. The wavelength window of the SE data varied from 271 to 1688 nm. The thickness of the ZnO film varied from 0 – 44.08 nm, obtained during the course of 51.17 minutes of the ALD process. The five major algorithms tested were Logistic Regression (LR), Support Vector Machines (SVM), Decision Tree (DT), Random Forest (RF), and k- Nearest Neighbors (kNN). Out of these, the kNN based approach performed the best, as it effectively predicted the thickness of the ALD ZnO films to within ± 1.5 nm with over 87 % accuracy. Further, this algorithm performed remarkably well, maintaining its accuracy even when SE data was downsampled by over 50 %. The prediction accuracy of the kNN algorithm was also sensitive to the spectral bandwidth in the SE data. The kNN improved its prediction accuracy to 88 % when analysis was restricted to a narrow spectral window spanning 271 – 745 nm. Taken together, these results highlight the effective use of ML-based algorithms in predicting optical thickness in thin films, and in showcasing the redundancy in SE data, once ML algorithms are adequately trained.

EL-Contributed On Demand-16 Photonic Crystals with a Narrow-Band Defect for the Infrared Spectral Range*, **V. Paige Stinson**, S. Park, M. McLamb,* University of North Carolina at Charlotte*; D. Childers,* US Conec, Ltd.*; T. Hofmann,* University of North Carolina at Charlotte

The fabrication of micro-scale, optically sensitive, structures using additive manufacturing techniques like two photon polymerization, for instance, has attracted significant attention in recent years. In two photon polymerization, sub-wavelength scale resolution is achieved in a non-linear process; thereby enabling the fabrication of a photonic crystal for the mid-infrared spectral range. It has been observed that the performance of photonic crystals fabricated using two photon polymerization is often impaired by layer thickness non-uniformity. We report on the design and analysis of one-dimensional photonic crystals with intentional defects to allow the quantification of thickness non-uniformities within one-dimensional photonic crystals in mid-infrared spectral range. The capability of photonic crystals to provide, tunable, narrow band transmission by the introduction of a defect has been demonstrated. The optical sensitivity of such a transmission peak to layer non-uniformity is explored here. Experimental demonstration, using FTIR microscopy, corroborates a strong correlation between stratified optical layer model calculations in which the expected impact of layer non-idealities is considered. These structures can provide an exceptionally efficient alternative to determining the layer non-uniformity of complex structures compared to conventional methods. We envision the use of FTIR microscopy-based characterization of infrared photonic crystals with defects for the process parameter optimization used for two photon polymerization fabrication.

Electronic Materials and Photonics Division
Room On Demand - Session EM-Contributed On Demand

Electronic Materials and Photonics Contributed On Demand Session

EM-Contributed On Demand-1 Non-Cu Interconnects - A Supply Chain Perspective*, **Jimmy Wang**, S. Odunuga, S. Sundararajan, S. Vyas, S. Semproni, S. King,* Intel Corporation*; W. Bodman, C. Chintakalaya, L. Bejarano, F. Sohail,* Arizona State University

Due to significant copper (Cu) resistivity size-effects and limitations in scaling the thickness of the associated high resistivity tantalum- (Ta) based diffusion barrier, there has been significant interest in identifying alternative metallization schemes with lower overall effective resistivities. To help identify potential metals with improved resistivity dimensional scaling properties relative to Cu, the product of electron mean free path (λ) and bulk metal resistivity (ρ_o) has been recently proposed as a potential figure of merit (FOM) based on the semi-classical Mayadas-Shatzkes and Fuchs-Sondheimer equations describing surface and grain boundary electron scattering in metals. Based on this FOM, over a dozen metals have been predicted to have the potential to outperform Cu at reduced geometries. However, there have been relatively few experimental investigations for some of the most promising metals identified (i.e. Ir, Rh, and Os) due to their prohibitive expense.

In this presentation, we address the limited information on platinum group resistivity scaling as well as the costs impeding their investigation and application. For the former, we have performed an expansive thin film resistivity literature search on all the low-$\lambda\rho_o$ FOM candidate metals to robustly establish the resistivity scaling performance of rare platinum group metals (PGMs). For the latter, we have examined the supply chain for PGMs from earth to usable form in semiconductor manufacturing (i.e. sputter target, organometallic precursor, …) to assess factors that influence pricing as well as search for opportunities to drive future cost reductions. Through the combined examination of a broader thin film resistivity dataset and associated supply chain considerations, we identify and suggest metals that may merit greater consideration as well as methods to potentially improving their economics for use in the semiconductor industry.

EM-Contributed On Demand-4 Designing Transition Metal Doped Lithium Fluoride Composite Cathode Materials For Li-Ion Batteries*, **Clifford Denize**, S. Danquah, J. Strimaitis,* Center for Materials Research Norfolk State University*; C. Bonner,* Chemistry Department Norfolk State University and Center for Materials Research Norfolk State University*; S. Pradhan, M. Behera,* Center for Materials Research Norfolk State University*; M. Bahoura,* Engineering Department Norfolk State University and Center for Materials Research Norfolk State University

Lithium-ion batteries are ever-present in our everyday lives in cell phones and laptops. Improving cathode materials is one of the ways to satisfy the need for a better energy storage solution. Developing new types of positive electrode materials to increase the cell voltage and capacity with improved stability is the best way towards the development of next-generation Li-ion rechargeable batteries. To achieve this goal, understanding the principles of the materials and recognizing the problems confronting the state-of-the-art cathode materials are essential prerequisites. Fluoride-based conversion high-energy cathode materials can be used to build next-generation lithium-ion batteries. FeF_3 andCuF_2 show a theoretical specific capacity value of 713 mAh/g, and 527.17 mAh/g, respectively. Similarly, Li-FeF_3 and Li-CuF_2 show a higher theoretical energy density of 900 Wh/kg. The insulating nature of LiF and limited splitting of LiF during charging are some of the challenges for lithiated fluorides.Lithiated fluorides also show some issues due to the lack of a presence of built-in Li source, poor capacity retention, and poor rate performance. To overcome these issues, we incorporate Fe, a transition metal with higher electrical conductivity, into LiF to form a composite material. A highly conformal and smooth surface area of transition metal lithiated fluoride composite thin film sample was achieved using pulsed laser deposition, both with and without annealing. To establish a baseline of performance, coin cells of slurry-made composites were created and compared to the thin-film counterparts. We expect the thin-film-based batteries to show a superior performance due to the improved uniformity and homogeneity of the composition and morphology. Structure and surface morphology of the thin film will be carried out using XRD, FESEM, and AFM. Electrochemical characterizations will include charge/discharge profile of battery assembly and cyclic voltammetry. This research finding will shed the light on the use of transition metal-doped LiF as promising cathode materials with improved rate performance and capacity retention.

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EM-Contributed On Demand-7 Physical Property Improvement of Atomic Layer Deposited Thin-film Interconnects*, **Ajit R. Dhamdhere**, B. Nie, H. Cho, H. Kim,* Eugenus, Inc.

Current electronic devices are gradually being based on 3-dimensional (3-D) complex structures of thin films to meet the growing demand for higher device density and speed. The high aspect ratio 3-D device structures together with rising thermomechanical stresses have put increasing demand for the alternative interconnect materials with superior mechanical and physical properties. Titanium Nitride (TiN) thin films are being widely used in the microelectronics industry as interconnects. Structural failure of TiN in 3-D high-aspect ratio electronic devices is a major concern for reliability and yield of electronic devices. The failure modes such as defects, bending, buckling have been observed to cause by inadequate physical properties of TiN film such as hardness, and modules of TiN film. In this work we show that by systematically adding SiN into TiN in the Atomic Layer Deposition (ALD) process, thin films of composite material TixSi(1-x)N grown show superior hardness and modulus compared to TiN thin films of similar thickness. ALD coatings of TixSi(1-x)N also have excellent step coverage and superior surface smoothness compared to TiN films.

TixSi(1-x)N films were deposited using Eugenus ALD deposition system by varying TiN:SiN ratio and SiN pulse duration. The films were characterized by various characterization techniques: ellipsometry, XRR, XRD, XPS, Nanoindentation, AFM, and TEM. It is observed that the deposited TixSi(1-x)N films maintained good crystallinity up to 10% Si doping. As Si doping % increase in the TiN matrix, the texture of TixSi(1-x)N thin films shift from (111) orientation to (002). Average crystallite size is measured by applying Scherrer analysis to the XRD peaks. The crystallite size decreases as Si content increased. By increasing Si percentage in the TixSi(1-x)N films improvement in hardness up to 38 GPa (TiN~18GPa) is observed. This increase in hardness is likely due to the grain-boundary hardening effect. The higher the Si%, the smaller the growth of TiN grains, hence higher the density of grain boundaries. Any movement of grains under external force becomes very difficult because of such network of grain boundaries, hence effectively rise in the hardness and modulus. Modulus of TixSi(1-x)N films increased as high as 350 GPa (TiN~170 GPa) by the addition of Si. TixSi(1-x)N films show excellent uniformity and good step coverage (> 90%) as measured using cross-sectional TEM images of HSC device structures. TixSi(1-x)N films (RMS Roughness 0.27 nm) show superior surface smoothness compared to TiN films (RMS Roughness 0.67 nm).

EM-Contributed On Demand-10 Wafer-Scale Fabrication of Nanostructured Carbon Thin Film-Based Electronic Devices*, **Zhigang Xiao**, L. Williams, J. Elam, A. Jones, Q. Yuan,* Alabama A&M University

we report an approach to grow nanostructured carbon thin films using a pair of AC-biased copper electrodes and fabricate carbon thin film field-effect transistors (CFETs). Graphite rod was evaporated in an ultrahigh-vacuum chamber using e-beam evaporation method, and nanostructured carbon thin films were grown between a pair of AC voltage-biased copper electrodes at a temperature of 400 ^{o}C. The electrodes with the carbon film were finally fabricated into the carbon thin film field-effect transistor (CFET), where the carbon thin film between the electrodes functioned as the channel of the transistor. The carbon thin film was analyzed with high-resolution tunneling electron micrograph (HRTEM), showing wiggling nanostructures in it. The electrical property of the fabricated CFET was measured before and after subject to an electrical breakdown, demonstrating much better electrical current (I)-voltage (V) curves and transfer characteristics with on/off current ratios of over 200 after the electrical breakdown process. The growth of nanostructured carbon film is novel, and the fabrication of CFET is compatible with the silicon-based semiconductor fabrication and can be wafer-scale.

EM-Contributed On Demand-13 Laser Induced Thermal Emission from Nickel Nanowires*, **Ana Silva**,* Cefitec, Physics Department, FCT, Universidade Nova de Lisboa, Portugal*; K. Pedersen,* Aalborg University, Denmark

Over the past two decades, there has been considerable progress in engineering the spectrum, directionality, polarization and temporal response of thermally emitted light using nanostructured materials [1].

Laser induced emission from self-assembled nickel wires, between 125-200 nm in diameter and tens of micrometers long, prepared by electrochemical deposition, emits strong infrared light when excited with a cw Ar^+ ion laser at 488 nm or a pulsed femtosecond Ti: Sapphire laser at 800 nm. The emission spectra from aggregates of Ni nanowires (NWs) heated by the absorption of laser light are investigated as a function of the power of the excitation laser. The emitted intensity increases exponentially with laser power which is taken as an indication of a thermal process. Through time response of the emission to a time varying laser excitation, the local temperature variation of the nanowires is determined. The radiation from the nanowires is describe by the classical Planck law modified by finite-size effects in nanoparticle emissivity. Similar emission spectra are observed for the two types of lasers. Theoretical modelling based on Mie's theory[2] and Planck's radiation law, using nanowires and nanocrystals of different sizes, is developed to fit the emission spectra.

The emission grows exponentially with pump power and over time the emission decays. The results point to thermal radiation process, modulated by size-effects, and strongly influenced by local plasmon modes (hot spots) that may lead to very large electric fields enhancements.

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Acknowledgments

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EM-Contributed On Demand-16 Wake up and Endurance of Ferroelectric $Hf_{0.5}Zr_{0.5}O_2$ on NbN and Nb*, **David Henry**,* Sandia National Laboratories*; S. Fields,* University of Virginia*; S. Smith, P. Davids,* Sandia National Laboratories*; J. Ihlefeld,* University of Virginia

This work investigates the wake up and endurance of ferroelectric behavior of atomic layer deposited (ALD) hafnium zirconium oxide (HZO) using reactively sputtered niobium nitride and niobium electrodes. With ferroelectricity in doped HfO_2now advancing into CMOS based devices, perturbations of the dopants has expanded from silicon into mixtures utilizing yttrium and zirconium and with electrodes ranging from platinum to tungsten and nitrides such as titanium nitride and tantalum nitride. New to the set of materials able to, in-part, stabilize the orthorhombic phase are other superconducting electrodes such as NbN and, in this work, Nb which we use to demonstrate stable ferroelectric behavior of $Hf_{0.5}Zr_{0.5}O_2$. With the atomic similarities between Ta and Nb, a natural extension the electrode materials' set to include NbN was explored in this work for the wake up and endurance properties.

Metal/Ferroelectric/Metal (MFM) capacitors tested at room temperature (RT) demonstrated ferroelectric behavior as determined by polarization vs. electric field (P-E) loops, remanent polarization, and capacitance vs voltage (C-V) measurements. Devices were made with either Nb or NbN bottom electrodes (BE), an ALD mediating layer of alumina, ALD HZO, and then a top electrode (TE) layer of NbN. Wake up cycling suggested a pristine state of tetragonal phase mixed with orthorhombic, as measured by P-E loops and C-V curves and moves to a more orthorhombic phase after modest wake up, for both a Nb and NbN BE. However, the Nb BE had only about half of the remanent polarization, 7 uC/cm^2, as to that of NbN BE at 13 uC/cm^2 suggesting that although an intermediate layer of alumina separated the HZO from the BE, the BE plays a critical role in HZO phases and electrical performance. Further, this work shows that with a NbN bottom electrode, a wake up of positive or negative pulses only contribute to full remanent polarization, 3 and 5 uC/cm^2 respectively whereas a full negative to positive of the same electric field generates a 7 uC/cm^{2}This work will discuss the implications of these wake up measurements, discuss life time cycling of these devices and compare to other electrodes.

Understanding the wake up and endurance of ferroelectric HZO on superconducting electrodes play into the exciting field of integration of ferroelectric thin films with superconducting films.

**EM-Contributed On Demand-19 Flexible Transition Metal Dichalcogenide Devices for Environmental Sensors and Energy Harvesting*, Alwin Daus*, *K. Nassiri Nazif, S. Vaziri, A. Khan, R. Grady, V. Chen, C. Bailey, H. Lee, C. Koroglu, K. Brenner, K. Schauble, A. Kumar, K. Saraswat, E. Pop,* Stanford University

Atomically thin transition metal dichalcogenides (TMDs) show promise for flexible devices such as sensors, energy harvesters and nanoelectronics [1-3], because they can detect factors important for environmental sensing such as temperature, humidity, gas, pressure and light [1, 2]. Furthermore, nanoscale TMD field-effect transistors (FETs) enable low-power processing of sensor data and wireless communication like radio-frequency identification [3]. We recently developed a novel transfer process for TMDs, enabling high-performance flexible nanoscale FETs [4]. In this work, we employ this transfer process to demonstrate monolayer MoS_2 temperature sensors and multilayer WSe_2 solar cells.

We have previously found that gated monolayer MoS_2 exhibits a high temperature coefficient of resistance (TCR) of +0.27 %/K compared to ultrathin metal films [5], and could enable sensors with low thermal mass due to their three-atom thinness. Here we fabricate flexible two-terminal (ungated) monolayer MoS_2 temperature sensors and obtain even larger (in absolute value) but negative TCR of -1.8 %/K between 30°C and 80°C. Preliminary analysis indicates that here space-charge limited current with shallow traps leads to the negative TCR, rather than phonon scattering causing a positive TCR in gated MoS_2. Furthermore, the sensors reveal a rapid real-time response of at least 150°C/min (limited by our heater stage) and reversibility.

In addition, the excellent optical absorption properties of TMDs and their near-ideal band gaps for single-junction and tandem solar cells (with Si) make this technology attractive for powering Internet-of-Things sensors at an ultrahigh specific power (>50 kW/kg), especially in wearables and environmental sensing systems [2, 6, 7]. We fabricated flexible WSe_2 solar cells with graphene top electrodes and MoO_x doping/passivation layer, where the whole active material is embedded within the flexible substrate, enabling a vertical cell architecture. We achieve a record-high power conversion efficiency of ~5%, while stable under mechanical bending to a radius of 4 mm. Concluding, this work provides important ingredients for flexible electronic systems where all active components benefit from the unique properties of atomically thin TMDs.

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**EM-Contributed On Demand-22 2020 AVS Graduate Research Award Talk: Monolithic Integration of Crystalline III-Vs on Amorphous Substrates using a Combination of Epitaxial and Non-epitaxial Methods*, Debarghya Sarkar*[1]*, R. Kapadia,* University of Southern California

A primary challenge for 3D integration and flexible electronics is the ability to integrate high performance devices at temperatures limited by the thermal budget of the substrate or pre-existing device layers. Present approaches mostly involve hybrid bonding techniques where epitaxial films are first grown on lattice-matched substrates and then transferred to the host substrate at a device scale, circuit scale, chip scale, or wafer scale. Although the devices made using these approaches are of excellent quality, this approach is usually limited by cost, time, limited materials, and scalability perspectives. Monolithic integration approaches attempt to directly grow materials on the host substrate, but device performance is usually poor from solution-based or vapor-phase grown semiconductors on non-epitaxial substrates which give submicron-scale grain polycrystalline films. Here we show results from a liquid-vapor-phase growth approach, referred to as Low Temperature Templated Liquid Phase (LT-TLP) growth. Templates of group III materials capped with SiO_2 are first realized on the non-epitaxial substrate by lithography, evaporation, and liftoff methods. These are then heated in the growth furnace at the intended growth temperature (between 200 to 400 ^{0}C), and group V precursor is introduced in the gas phase as pre-cracked V-hydride. The flux of the group V precursor is controlled to ensure single nucleation in each template, which grows with time to yield single crystal III-V in each template, confirmed by electron backscatter diffraction (EBSD) imaging. Photoluminescence measurements for different growth temperatures give an optimal growth window of 280-320 ^{0}C, where optoelectronic quality is found to be comparable to single crystal commercial wafer. InAs grown at 300 ^{0}C shows room temperature mobility of ~6000 cm^2/V-s. Comparing the highest electron mobilities reported from different material families grown directly on amorphous dielectric surfaces, it is seen that TLP III-Vs have the best mobilities, with LT-TLP InAs being about 2 orders of magnitude higher than the majority. These low temperature growths have been performed on rigid dielectric substrates like SiO_2 and HfO_2, as well as on flexible polyimide. Further, these high quality single crystalline mesas have been used as growth seeds for epitaxial films by MOCVD. Growth parameter variations are studied to obtain the best MOCVD InP-on-TLP InP morphology and optoelectronic properties. This potentially opens up a scalable and cost-effective method of integrating high quality III-V materials and devices on inexpensive amorphous dielectric surfaces for 3D integration.

**EM-Contributed On Demand-25 Evaluation of the Near-Zero Temperature Coefficient of Resistivity (NZ-TCR) of ALD $TiSi_xN$ Films*, Corbin Feit*, *S. Berriel* , University of Central Florida*; A. Dhamdhere, H. Kim, B. Nie, S. Chugh, S. Rothi, N. Mukherjee,* Eugenus, Inc.*; P. Banerjee,* University of Central Florida

Atomic Layer Deposition (ALD) of ternary $TiSi_xN$ leads to nanocomposites of metallic TiN atomically mixed with insulating Si_3N_4. Formulating $TiSi_xN$ films with various Ti:Si ratios lead to the emergence of a temperature regime where resistivity is independent of thermal drift, denoted as near-zero temperature coefficient of resistivity (nz-TCR).[1] Further, the ease with which nanocomposites of $TiSi_xN$ can be deposited using ALD offer precise tunability in Ti:Si ratio, thickness, mass density, crystallinity and electrical properties.

Recently, our group explored $TiSi_xN$ films deposited using a Eugenus® 300 mm commercial QXP mini-batch system by modulating the ratio of Ti and Si precursors with NH_3 as a co-reactant.Si-content was varied from 0 at % (pure TiN) to 24.2 at % Si while maintaining thickness ~ 140 nm. The X-ray reflectivity and grazing incidence X-ray diffraction measurements showed a reduction in film density and transition from nano-crystalline to pure amorphous phase with increase in Si-fraction. Spectroscopic ellipsometry revealed the optical constants, composition, and electrical resistivities and were supported by X-ray photoelectron spectroscopy and electrical measurements. Room-temperature resistivity measurements show an increase in film resistivity with increasing at % Si. Temperature-dependent Van der Pauw measurements found a nz-TCR of -23 ppm K^{-1} in the temperature range of 298 K – 398 K and at 3.4 at % Si content.

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[1] **AVS 2020 Graduate Student Awardee**

We have now discovered that an at % Si = 3.0% induces a nz-TCR of -5.7 ppm K^{-1} from 80 K – 420 K – one of the best reported nz-TCR values for ALD thin films. Fine tuning the at % Si in $TiSi_xN$ films, possible only via ALD, significantly elongated the temperature window of nz-TCR behavior. Mapping the local conductivity of individual grains through conductive atomic force microscopy (c-AFM) indicated higher resistance at the grain boundaries. The local composition at the grain boundaries may play a major role in determining the nz-TCR behavior of $TiSi_xN$ films. In addition, variable temperature Hall effect measurements were performed to provide deeper insights into the nz-TCR mechanism, decoupling carrier concentration from carrier mobility effects while determining film resistivity.

Compared to other nz-TCR films, which are deposited using physical vapor deposition techniques, ALD based nz-TCR films presents a unique synthesis platform for interconnect technology in topologically complex, 3D devices, circuits and sensors that undergo large temperature variation during operation but need to maintain stability in their electrical characteristics.

EM-Contributed On Demand-28 Berry Curvature Memory Through Stacking Transitions in Topological Semimetals*, Jun Xiao,* Stanford University*; Y. Wang,* UC Berkeley*; H. Wang,* Texas A&M University*; C. Pemmaraju,* SLAC National Accelerator Laboratory*; S. Wang,* UC Berkeley*; P. Muscher, E. Sie, C. Nyby, T. Devereaux,* Stanford University*; X. Qian,* Texas A&M University*; X. Zhang,* UC Berkeley*; A. Lindenberg,* Stanford University

Quantum materials with novel phases of matter are the key building blocks of energy-efficient quantum electronics and powerful quantum computation. Exploiting control of those materials is fascinating to achieve new functionalities and information algorithms in future quantum devices. Quantum nanomaterials like layered materials have revealed many exotic properties such as extremely large magnetoresistance (MR)[1], type-II Weyl electron transport, and diverging Berry curvature[2]. On the other hand, the nature of layered materials leads to ultra-large tunability of physical properties via external stimuli.

Here we report the manipulation of quantum geometrical properties in a ferroelectric semimetal (WTe_2) belonging to layered Weyl materials (Fig. 1). With such control and various characterization means, we observed substantial modulation in optical and electrical responses associated with the unique stacking orders in such exotic ferroelectric semimetal. Further nonlinear Hall transport measurements show the observed transitions are locked with the variation of topological and geometrical property (Fig. 2). Our findings demonstrate a new low-energy cost, electrically controlled topological memory in the atomically thin limit[3].

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EM-Contributed On Demand-31 Metal-Semiconductor Contacts to β-Ga_2O_3: Dependence on Metal Work Function and Crystallographic Surface Plane*, L. Lyle, K. Jiang, E. Favela, Y. Yao,* Carnegie Mellon University, USA*; K. Das,* North Carolina State University*; Z. Galazka, A. Popp,* Leibniz Institute for Crystal Growth, Germany*; **Lisa Porter**,* Carnegie Mellon University, USA

Because of its ultra-wide bandgap (~4.8 eV), full range of n-type doping, and availability as single-crystal substrates produced from melt-growth methods, β-Ga_2O_3 is being intensively pursued for electronic devices that could substantially increase device operating limits for voltage and power. The successful device development of any semiconductor technology requires the ability to produce suitable ohmic and rectifying (Schottky) contacts.In the case of β-Ga_2O_3, most metals tend to naturally form Schottky contacts, whereas few metals have been established as ohmic contacts to this semiconductor.Our investigations of numerous metal contacts have also shown significant differences for different Ga_2O_3 surfaces.For example, Schottky barrier heights of metals on (-201) Ga_2O_3 showed little to no dependence on the metal work functions, suggesting significant Fermi level pinning.In contrast, Schottky barrier heights for metals on (100) Ga_2O_3 showed a strong correlation with the metal work functions: e.g., the slope S was 0.96 and 0.61 for the I-V and C-V determined Schottky barrier heights, respectively.For ohmic contacts to Ga_2O_3, we found that the metal work function is not a dominant predictive factor; whereas interfacial reactions and contact morphology play important roles in ohmic contact formation.Results and analyses from electrical measurements of many different metals that formed ohmic or Schottky contacts to (-201) and (100) β-Ga_2O_3 will be presented and discussed.

EM-Contributed On Demand-34 Effect of Cobalt Doping on Structural, Magnetic and Ferroelectric Properties of Bismuth Ferrite Thin Films Grown Epitaxially on $SrTiO_3$ (001)*, **Chhatra Raj Joshi**, M. Acharya, M. Seikh,* The University of Alabama*; J. Plombon, U. Alaan, T. Gosavi,* Intel Corporation*; A. Gupta,* The University of Alabama

$BiFeO_3$ (BFO), the most extensively studied room temperature multiferroic material with Néel temperature T_N ~ 640K and Curie temperature T_C ~ 1100K, shows strong coupling between antiferromagnetic and ferroelectric order parameters. BFO could be a potential candidate to be used in magnetoelectric logic and memory devices due to the presence of this strong coupling. However, overcoming high leakage current, high switching voltage and low remnant magnetization are the biggest challenges for its device applications. Materials with lower coercive voltages V_c are desired to reduce the operating voltage for lower power consumption as well as to avoid thermal decomposition of the material in thin film form. With Fe-site substitution by magnetic element Co, the spin structure of BFO is indeed modified and a canted collinear phase with weak ferromagnetic moment at room temperature is stabilized. Also, doping with Co can lead to changes in the crystal structure that possibly affect its ferro/piezo-electric properties. $BiFe_{1-x}Co_xO_3$ (xBFCO) with different x values could be a suitable material with enhanced magneto-electric properties for device application.

Epitaxial films of multiferroic $BiFe_{1-x}Co_xO_3$ ($0 \le x \le 0.35$) are grown on $SrTiO_3$ (001) and $SrRuO_3$ buffered $SrTiO_3$ (001) using pulsed laser deposition technique. The effect of Co substitution on the crystal structure, magnetic properties and piezo/ferro electric properties are investigated. The XRD analysis indicates that the phase-pure xBFCO has been synthesized for ($0 \le x \le 0.35$) without any secondary impurity phases. As the Co concentration increases, the films are stabilized as tetragonal phase $BiCoO_3$-like structure. The semi-empirical Kay-Dunn scaling law of coercive voltage (V_c) with thickness (t) ($V_c \sim t^{1/3}$) for different concentrations of cobalt are studied using piezo force microscopy (PFM) technique. Here we demonstrate that within the rhombohedral structure, systematic reduction of the coercive voltage can be achieved by increasing substitution of Fe by cobalt on BFO. These results suggest a possible pathway to realize BFO-based non volatile magneto-electric memory devices with relatively lower operating voltages. Moreover, to understand the effect of Co doping on the structural, magnetic and the electronic properties, we have performed theoretical calculations using density functional theory (DFT). The results indicate that a reduction in unit cell volume, enhancement in net magnetization and reduction in the band gap can be achieved by Co doping of BFO.

EM-Contributed On Demand-37 High-Quality Molybdenum Nitride Schottky Diodes to *n*-Type Gallium Nitride*, Alex Molina,* *I. Campbell, T. Walter, A. Agyapong, S. Mohney,* Pennsylvania State University

Although silicon (Si) currently dominates the semiconductor industry, its small band gap (1.1 eV) limits its maximum operating temperature, restricting its use in high-temperature, high-power devices. Gallium nitride (GaN) is an attractive semiconductor with its wide bandgap (3.4 eV), high electron mobility, large critical breakdown field, and thermal stability. While the semiconductor itself can endure harsh operating conditions, the reliability of the metal/semiconductor contacts can be a limiting factor for its use. Schottky contacts should provide a high barrier height and low reverse leakage current, and they must be electrically stable over the lifetime of the device.

The MoN_x/*n*-GaN Schottky diode was chosen for study because of the reported high work function of MoN_x (5.33 eV)[1] and its conductive and refractory nature. It is also reported to be in thermodynamic equilibrium with GaN[2]. Films were deposited by plasma atomic layer deposition and were examined by x-ray photoelectron spectroscopy (XPS), grazing incidence x-ray diffraction (GIXD), and transmission electron microscopy (TEM) with energy dispersive spectroscopy (EDS) to determine their composition and structure. TEM reveals an abrupt interface between MoN_x and *n*-GaN with a cubic phase that is further confirmed with GIXD and EDS. XPS show a significant amount of carbon within the cubic phase. The barrier heights were investigated using current-voltage (I-V) and capacitance-voltage (C-V) measurements. Both techniques demonstrated that the barrier height increased after an anneal at 600°C for 5 min, yielding a barrier height of 0.87 eV with an ideality factor of 1.02 by I-V measurements, while the C-V measurements revealed a barrier height of 0.94 eV. Rectifying behavior was maintained upon annealing in N_2 at 700°C.

Future work will involve stress testing followed by materials characterization to provide more information on stable metallizations for high-power GaN devices. This work was funded by the Office of Naval Research under Grant N000141812360, distribution A, approved for public release, distribution is unlimited (DCN# 43-8038-21).

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EM-Contributed On Demand-40 Area-Selective Deposition/Patterning of Boron Carbide Layers with Atomic Layer Deposition*, **Raja Sekhar Bale**, R. Thapa, L. Dorsett, S. Wagner, A. Caruso,* Department of Physics and Astronomy, University of Missouri- Kansas City*; J. Bielefeld, S. King,* Intel Corporation*; M. Paquette,* Department of Physics and Astronomy, University of Missouri- Kansas City

The semiconductor industry is pushing its boundaries in device scaling technology 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, Si-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 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 metal/dielectric deposition of boron carbide using layer-by-layer methods. X-ray photoemission spectroscopy (XPS), scanning electron microscopy (SEM) and atomic force microscopy (AFM) techniques are employed for characterization and imaging of the resulting surfaces.

EM-Contributed On Demand-43 Carbon Nanotube Templated EUV Windows*, **Scott Olsen**, D. Allred, S. Turley, R. Vanfleet,* Brigham Young University

Extreme Ultraviolet (EUV) windows are difficult to achieve due to high opacity of materials in the EUV range. Traditional hollow cathode sources are windowless. However, windowless source are not acceptable in many applications due to downstream instruments needing low pressures to operate. We have developed carbon nanotube (CNT) templated structures with high open area up to 85% for good optical transmission and a corresponding low conductance less than 6 L/s to restrict gas flow. The structure was developed using common lithography techniques for patterning and CVD for CNT growth and infiltration. Observing the intensity distribution of a helium hollow cathode plasma for visible and 58.4 nm at 0.25-2 torr and 75-1325 mA through an aperture provides an empirical model of the light source. The intensity distribution due to a CNT structure mounted to the aperture is determined and discussed.

EM-Contributed On Demand-46 Low Temperature Fabrication of Cathodes for Lithium Thin Film Batteries*, **Wyatt Tenhaeff**,* University of Rochester

With the continued evolution of microelectronic devices and their miniaturization, energy storage devices with reduced dimensions, especially Li-ion batteries, are critically needed. Solid-state lithium thin-film batteries (TFBs) offer exceptional energy storage performance with high energy density, long cycle life, and enhanced safety. The current-state-of-the-art thin film cathode, $LiCoO_2$ (LCO), offers a charge storage capacity of 67 μAh cm^{-2} μm^{-1} (equivalent to 135 mAh g^{-1}). Because the overall energy density of TFBs is largely determined by the thin film cathode, developing materials with higher specific capacity is a key strategy to enhancing the stored energy. In this talk, our efforts to engineer novel, energy dense thin film cathodes prepared at low temperatures will be discussed.

The first project to be discussed utilizes polymeric charge-transfer complexes. These complexes are formed through the vapor phase infiltration of I_2 or ICl into poly(4-vinylpyridine) (P4VP) films prepared by initiated chemical vapor deposition (iCVD). iCVD enables room-temperature synthesis of well-defined films directly on the surface of Pt current collectors. After infiltration with I_2 or ICl, the cathodes are coated nominally with 1 μm of lithium phosphorous oxynitride (LiPON) electrolyte and an evaporated Li metal anode. The P4VP-I_2 and P4VP-ICl deliver capacities of 8.7 and 36.2 μAh cm^{-2} μm^{-1}, respectively, with an average voltage of 2.2V and 3.15V. The cathodes appear to be irreversible under normal operating conditions, limiting their application to primary electrochemical cells. However, it has been shown that these cathodes are readily prepared on flexible, temperature sensitive substrates, as well as complex, three dimensional architectures, which should allow them to be readily integrated into wearable, low cost devices and enable additional energy-intensive applications.

In the second project, a class of lithium metal oxide cathode materials are prepared by RF magnetron sputtering and incorporated into solid state thin film batteries (consisting of LiPON electrolyte and Li metal anode). Charged to 4V vs. Li/Li$^+$, specific capacities in excess of 110 mAh cm^{-2} μm^{-1} have been achieved, which is 64% larger than state-of-the-art LCO cathodes. When cycled at a rate of 0.6C (100 minutes for charge/discharge), 83% of the maximum capacity is retained. Moreover, the cathodes are highly reversible with coulombic efficiencies in excess of 99.8%, resulting in greater than 94.7% capacity retention over 100 galvanostatic charge/discharge cycles. Efforts to further enhance rate performance and cycle lives will be discussed, in addition to demonstrations of these cathodes on flexible, polymeric (temperature sensitive) substrates.

EM-Contributed On Demand-49 Pressure Increases Power Conversion Efficiency and Interlayer Diffusion in Perovskite Solar Cells*, **Deborah Oyewole**, J. Hinostroza-Tamayo, Z. Mutton, O. Oyewole, W. Soboyejo, N. Burnham,* Worcester Polytechnic Institute

To be a commercial success, perovskite solar cells must not only be efficient relative to their cost, but also stable over time. Recent work demonstrates that the power conversion efficiency of methylammonium-chloride-lead-iodide ($MAPbI_{3-x}Cl_x$) perovskite solar cells (PSCs) can be increased by approximately 40% by applying up to 7 MPa of pressure. [1] The accompanying SEM images before and after the application of pressure show improved contact at the interface between the compact TiO_2 and the fluorine-doped tin oxide.In subsequent layer-by-layer deposition, the interface roughnesses were in the range of 10 to 40 nm RMS as measured by AFM.Initial results from energy dispersive spectroscopy demonstrate significant interlayer diffusion and cracking in pressurized solar cells, particularly of iodine, lead, and tin, but limited diffusion and much lower incidence of cracking in unpressurized devices.The devices with higher diffusion and cracking had lower power-conversion efficiencies and lower stability.[2]Diffusion was also studied as a function of annealing time and temperature.We will discuss the competition between improved contact and diffusion/cracking in pressurized PSCs and their implications for the improvement of long-term power conversion efficiency.

54. Oyelade, O. V., et al. "Pressure-Assisted fabrication of perovskite Solar cells." *Scientific reports* 10.1 (2020): 1-11.
55. Oyewole, D., et al. “Pressure-Induced Void and Crack Closure Improve the Photoconversion Efficiency and Stability of Perovskite Solar Cells,” submitted

EM-Contributed On Demand-52 Enhanced Luminescence of Sio$_X$ /Sio$_2$ Multilayers Structures Obtained by Sputtering Technique*, **Alma Lizet Valdez**, K. Monfil,* Research Center of Semiconductor Devices, Mexico*; A. Morales,* bNational Institute of Astrophysics, Optics and Electronics, Mexico*; F. Morales,* Center investigated of optics A.C, Mexico*; F. Uribe, J. Luna, Z. Hernández,* Research Center of Semiconductor Devices, Mexico*; A. Muñoz,* Electronics Faculty. Meritorious University Autonomous of Puebla, Mexico

In particular, the non-stoichiometric silicon oxide (SiO_x) has been proposed as a cheap and effective alternative to develop ultraviolet absorbers or light emitters. SiO_x films can be deposited by several deposition techniques but they can be obtained at Room Temperature by Sputtering deposition technique. New devices based on SiOx films include different structures of stacked films like multilayers or superlattices.

This work presents a study of the optical, structural and electrical properties of non-stoichiometric silicon oxide on silicon oxide (SiO_x /$SiO_{2)}$ multilayers obtained by sputtering deposition technique. Non-stoichiometric silicon oxide films were deposited using a combination of Silicon and quartz (SiO_2) targets. Therefore, the study of the optical and structural properties of non-stoichiometric silicon oxide films by using silicon and silicon oxide targets is an interesting route for the design of optoelectronic devices based on Silicon technology. The SiO_x/SiO_2 multilayer structure was formed by five stacked bilayers with the different power application on target silicon.All samples were deposited on silicon substrates with low resistivity.

One of the main achievements to produce SiO_x /SiO_2 multilayers structures with different silicon excess, was to control the variation of the power on the Silicon target and keeping constant the power on silicon oxide target.In this case, electroluminescent devices were developed with multilayers structures involving silicon nanocrystals, to reduce the energy barrier for conduction between the silicon oxide layers and silicon nanocrystals. According to our results, the threshold voltages to obtain a visible electroluminescence were reduced in comparison with previous reports. Therefore, it could be better to use a multilayer that uses SiOx / SiO_2 mixture layers with high photoluminescence to reduce the energy barrier for conduction between nanocrystals and consequently lower voltages would be required for carriers' injection.

EM-Contributed On Demand-55 Optimized Deposition Conditions of Silicon Rich Nitride Obtained by Lpcvd to Achieve Down-Conversion Effect as Uv Absorption Coating on Solar Cells*, **Francisco Uribe-González**, K. Monfil, M. Domínguez,* Research Center of Semiconductor Devices, Meritorious University Autonomous of Puebla, Mexico*; M. Moreno,* National Institute of Astrophysics, Optics and Electronics, Mexico*; A. Muñoz,* Electronics Faculty. Meritorious University Autonomous of Puebla, Mexico*; J. Hernández, A. Salazar,* Research Center of Semiconductor Devices, Meritorious University Autonomous of Puebla, Mexico

The research trend on new materials and alternatives to improve energy generation devices, includes the synthesis and development of absorbent coatings. In particular, silicon solar cells can be optimized with coatings capable of capturing more or less energetic wavelengths than silicon can assimilate, this could be possible through silicon rich nitride (SRN). Silicon nitride has been used in many industry sectors as a protective coating, but the SRN also has convenient optical characteristics to achieve an improvement on efficiency of silicon solar cells keeping in mind the best cost-efficiency. This can be achieved by the down conversion effect. In this work, we propose an optimization on the deposition conditions of SRN films obtained by LPCVD to achieve the down-conversion effect. SRN films were obtained using NH_3 mixed with SiH_4 as precursor gases with a ratio of R_{on} between 4 and 80, the temperature was varied from 600°C to 720°C and thermal annealing was applied to some samples to compare with as-deposited films. Ellipsometry measurements showed that thickness and the refractive index can be well controlled by the gases ratio and deposition temperature. Fourier transform infrared (FTIR) spectra showed characteristic peaks of Si-N matrix and N-H vibration modes. The images of AFM showed that surface roughness morphology can be also affected by the deposition temperature. Energy dispersive spectroscopy measurements were obtained to estimate the SRN films composition, the results showed a silicon enrichment dependence on temperature. SRN films showed a clear photoluminescence (PL) at room temperature (RT), the main band was located between 380 to 650 nm. PL emission was related to donor acceptor decays between traps promoted by defects.

The optical, structural and morphological characteristics SRN films showed a clear dependence on the deposition time, the ratio of the precursor gases and the deposition temperature. Suitable refractive index, surface roughness and PL emission were obtained with a flow ratio of 4 and deposition temperature of 700 °C. These deposition conditions assure convenient optical characteristics of SRN films to achieve down conversion effect and they suppose a low influence on diffusion of PN junctions when SRN is used as UV absorption coating.

Keywords: Silicon rich nitride, LPCVD, Photoluminescence

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EM-Contributed On Demand-58 Interfaces between III-V Semiconductors and High-K Dielectrics: Opposite Requirements for MOSFET, Ferroelectrics, and Resistive Ram Applications*, A. Irish, A. Troian, R. Atle, A. Persson, S. Mamidala, K. Persson, G. D'Acunto, L. Wernersson, M. Borg, **Rainer Timm**,* Lund University, Sweden

Novel computation challenges including neuromorphic networks, memory-centric computation, machine learning, or steep-slope transistors require to go beyond traditional MOSFET architecture and instead explore high-k thin films for ferroelectric or resistive random access memory (RRAM) technology. Typically, such ferroelectric or RRAM thin films are deposited on Si substrates, which still is the standard material within electronics industry. However, III-V semiconductors such as InAs or InGaAs offer a much higher charge carrier mobility and more flexibility for low-power applications. We are investigating HfO_2 RRAM and $Hf_{1-x}Zr_xO_2$ (HZO) ferroelectric thin films on InAs and InGaAs substrates and gate-all-around nanowire structures, the latter for reaching ultimate electrostatic control. In order to obtain state-of-the-art device performance and outperform silicon technology, we need to thoroughly understand and optimize the materials properties of the III-V/high-k interface.

Previously, we performed various synchrotron X-ray photoemission (XPS) studies of InAs/HfO_2 and InAs/Al_2O_3 interfaces of MOSFET devices, where we analyzed the role of different As sub-oxides and defect states, obtained As-oxide and In-oxide interface depth profiles, and also looked at interfacial thermal oxides. It turned out that best device performance was reached with as little interfacial oxide as possible. By implementing atomic layer deposition of HfO_2 at an ambient-pressure XPS synchrotron beamline, we could even reach perfect self-cleaning and reveal new insights on the surface chemistry involved in the self-cleaning mechanism.

Here, we will present systematic XPS and X-ray absorption spectroscopy (XAS) results together with electrical device data of ferroelectric HZO and RRAM HfO_2 films on InAs and InGaAs. In contrast to the MOSFET applications, we observe that a certain thickness and composition of interfacial oxide is required in order to obtain RRAM or ferroelectric functionality. In the case of RRAM nanowires, we find a critical dependence on the type of oxide deposition method and parameters, since these determine the amount of oxygen vacancies that influence the conductive filament formation. Furthermore, we obtain an inhomogeneous depth profile of the interfacial oxide. For ferroelectric HZO films with a thickness of down to 4 nm, oxygen vacancies and defects at the interfaces both to the top metal electrode and to the InAs substrate turn out to be critical for device performance and polarization endurance. A combined and interactive materials science and electrical device processing approach is needed to optimize these complex interface structures.

EM-Contributed On Demand-61 Atomic Scale Defects Generated by High-Field Gate Stressing in Si/SiO_2 Transistors*, **Stephen Moxim**, F. Sharov,* The Pennsylvania State University*; D. Hughart, G. Haase,* Sandia National Laboratories*; P. Lenahan,* The Pennsylvania State University

An understanding of time-dependent dielectric breakdown (TDDB) in SiO_2 gate dielectrics has long been of great interest. Several models have been proposed involving the generation of oxide traps which eventually form a percolative leakage path through the dielectric. However, little direct experimental evidence about the traps exists. Electrically detected magnetic resonance (EDMR), and near-zero-field magnetoresistance (NZFMR) can provide this atomic scale information in real devices. We present EDMR and NZFMR studies of defects generated during the high-field gate stressing of Si/SiO_2 MOSFET arrays. Our studies substantially extend earlier resonance studies which were only able to identify one interface defect [1,2]. We subject our devices to gate stressing conditions and periodically interrupt the stress to measure interface recombination current, and spin-dependent interface recombination (SDR) current via EDMR and NZFMR. A nearly perfect correspondence between recombination current and SDR response is found at all stressing conditions. Interface state buildup occurs more rapidly early in the device lifetime, and more slowly as time goes on. By performing EDMR at multiple magnetic field orientations, we identify the stress-induced interface defects as P_{b0} and P_{b1} centers, dangling bond centers at the Si/SiO_2 interface. In addition, we observe a weaker SDR response in lower temperature (200K) measurements due to traps created within the oxide, likely oxide silicon dangling bonds known as E' centers. Of particular interest, we find that the NZFMR response exhibits subtle changes in lineshape after different durations of gate stress, which we attribute to changes in the population of hydrogen in the vicinity of the Si/SiO_2 interface.

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Sandia National Laboratories is 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.This paper describes objective technical results and analysis. Any subjective views or opinions that might be expressed in

the paper do not necessarily represent the views of the U.S. Department of Energy or the United States Government.

EM-Contributed On Demand-64 Ultrafast Switching of FeRh Memristors*, **Nicholas A. Blumenschein**, G. Stephen,* Laboratory for Physical Sciences*; C. Cress, S. LaGasse,* United States Naval Research Laboratory - Electronics Science and Technology Division*; A. Hanbicki,* Laboratory for Physical Sciences*; S. Bennett,* United States Naval Research Laboratory - Materials Science and Technology Division*; A. Friedman,* Laboratory for Physical Sciences

FeRh is widely studied because of its novel temperature-dependent antiferromagnetic (AFM) to ferromagnetic (FM) phase transition. This AFM-FM phase transition, which is accompanied by a significant change in resistivity, occurs at a critical temperature that can be fine-tuned over a wide range through substitutional doping, strain, and patterning.[1,2] Because the transition is temperature-dependent, the state can be manipulated *via* Joule heating. Recent reports show the AFM-FM transition occurs on a sub-picosecond timescale, a range appropriate for switching applications where operating speeds should be in excess of GHz frequencies. In this work we demonstrate ultrafast memristive switching of FeRh wires. The thermally-induced AFM-FM transition was evaluated using two-terminal devices consisting of an FeRh wire and metal contacts. By using FeRh wires of varying dimensions, we were able to identify geometrical dependencies and found the AFM-FM transition temperature scaled with both current density and wire length. Pulsed I-V measurements were used to investigate the dynamic Joule heating effects, including the device switching speed and resulting power switching losses accompanying the AFM-FM transition. The upper bound of our device switching speeds, measured to be near 300 nanoseconds, was limited by measurement equipment limitations, not the material system. The performance of this rudimentary device is comparable to other phase change memory technologies with more intricate device architectures. FeRh could be the basis for a very fast, phase-change approach to future computing.

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EM-Contributed On Demand-67 Innovative Approach and Study of Transparent Conducting Oxide as Channel Materials for the Fabrication of Thin Film Transistors*, **Kelsea Yarbrough**, S. Pradhan, M. Bahoura,* Norfolk State University

Photolithography has been the most widely used technique for semiconductor fabrication and large-scale mass production of silicon-based devices. By 2025, the photolithography equipment will have a market worth of $18 billion. Commercial, thin film transistors are developed using the process of photolithography. One technique we plan to introduce to fabrication TFT is 3D printing mask technique. 3D printed technology, commonly referred to as additive manufacturing, is a process used to reduce cost of various deposition techniques. 3D printed mask technology was used to deposit the active layer and the dielectric layer of our devices. The indium-free oxide-based channel material such as aluminum-doped zinc oxide (AZO) is the active material and can be fabricated on glass substrate or silicon for TFT application.High quality AZO thin films were grown using radio frequency (RF) sputtering technique and pulsed laser deposition on p-type silicon and glass for characterization purposes. The effect of Al content on zinc oxide crystal lattice were investigated by Atomic Force Microscopy (AFM), X-ray diffraction, Raman Spectroscopy, Ultra-violet visible spectroscopy, and Keithley 4200 Semiconductor Characterization System (SCS). AFM provided details information about the roughness, grain size, and surface morphology of thin films. FE-SEM measurement was performed to show cross sectional view of the fully developed thin film transistor. Raman Spectroscopy provided vibrational frequencies and a fingerprint of thin film used for the device fabrication. Finally electrical transistor characteristics were carried out using Keithley 4200 SCS provided including on/off ratio, mobility, and threshold voltage. The present work will provide valuable scientific input of AZO based active materials TFTs for the improvement of devices performance.

EM-Contributed On Demand-70 Epitaxial Growth of Donor and Acceptor Doped β-Ga_2O_3 by Magnetron Sputter Deposition*, **Adetayo Adedeji**,* Elizabeth City State University*; J. Lawson, A. Reed, S. Pacley, J. Merrett,* Air Force Research Lab

High quality β-Ga_2O_3 films were deposited on various single crystal β-Ga_2O_3 substrates by magnetron sputtering. Doping of the epilayers was achieved by co-sputtering a pure Ga_2O_3 target and Si, Sn, or Fe Si targets. The substrate temperature was 570°C during a 2-hour deposition in Ar/O_2 gas mixtures (5% O_2 by flow rate). Substrate orientations used were (010) or (-201) and were either Sn-doped, unintentionally doped (Si doped in 10^{17} cm^{-3} range), or semi-insulating Fe-doped. Radio frequency power was applied to the Ga_2O_3 target while the dopant targets were sputtered with RF or DC power. A Si-doped sample was deposited using DC sputtering on a pure Si target. The sample thickness measured by ellipsometry was 187.2 nm. At the corners of 5 mm x 5 mm samples, Ti/Au contact metals were deposited by electron beam evaporation. The contacts were annealed in argon flow at 550°C. Room temperature Hall-Effect measurements indicated donor concentration of about 3 x 10^{19} cm^{-3}. The average sheet resistance, resistivity, and carrier mobility are 652 Ω/sq•, 1.23 x 10^{-4} Ω·m, and 19.1 cm^2/V·s respectively. Additional samples were produced with either no dopant, Fe, Sn, or Si targets. Fe-doped films were found to be non-conducting. High resolution x-ray diffraction (XRD) 2θ-ω, 2θ and rocking curve measurements were performed to determine the film crystallinity. Differences in crystallinity were observed based on Ga_2O_3 film doping and substrate choice. A small secondary (-201) Ga_2O_3 diffraction peak on 2θ-ω XRD scan for the un-doped Ga_2O_3 on (-201) Sn:doped Ga_2O_3, combined with minimal diffraction peaks on the 2θ scan and a secondary peak on the rocking curve scan, suggest predominately epitaxial growth. The XRD analysis for the Sn:doped on Ga_2O_3 on the unintentionally-doped Ga_2O_3 substrate were inconclusive. Further analysis will be done to determine whether the film is amorphous or homoepitaxial.

EM-Contributed On Demand-73 The Synthesis of $NbSe_2$ by Molecular Beam Epitaxy for Thermomagnetic Energy Conversion*, **Peter Litwin**, S. Akhanda, M. Zebarjadi, S. McDonnell,* University of Virginia

The synthesis of high-quality $NbSe_2$ thin films is of significant interest for potential applications in thermomagnetic energy conversion. Molecular beam epitaxy (MBE) is a promising route towards this aim as it provides fine control over growth conditions. For thermomagnetic energy conversion, the metallic 2H phase of $NbSe_2$ is desired. However, a number of competing phases are found to form during synthesis by MBE and likely include metastable phases, such as semiconducting 1T-$NbSe_2$. It has been previously reported in literature that metastable 1T-$NbSe_2$ forms at higher temperatures than the 2H phase. Conversely, higher growth temperatures are potentially beneficial for growing high-quality 2H-$NbSe_2$ because of improved adatom mobility that results in better crystalline quality. We will report on an investigation of the competing effects of crystal quality versus mixed phase growth with a goal of optimizing growth conditions for thermomagnetic energy conversion. In-situ X-ray photoelectron spectroscopy (XPS) and reflection high energy electron diffraction (RHEED) will be performed to analyze the intrinsic chemical composition and growth mode of the synthesized material prior to atmospheric exposure. Ex-situ Raman spectroscopy will aid in phase identification. In order to obtain the Nernst coefficient, which quantifies the material's ability to generate thermomagnetic power, ex-situ measurements will be carried out on $NbSe_2$ films grown on insulating muscovite.

EM-Contributed On Demand-76 Scaling of Atomic Layer Deposited Dielectrics on UV-O_3 Functionalized WSe_2*, **Maria Gabriela Sales**,* University of Virginia*; S. Najmaei,* Army Research Laboratory*; S. McDonnell,* University of Virginia

WSe_2 offers fundamentally unique charge carrier and transport properties compared to other transition metal dichalcogenides (TMDCs), such as its propensity for p-type doping and its enhanced spin-orbit coupling. These qualities make WSe_2 a promising channel candidate for a multitude of different applications, including field effect transistors (FETs) and low power memory devices. For integration in an electronic device, TMDCs such as WSe_2 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. Atomic layer deposition (ALD) is the conventionally used technique for dielectric deposition, but it has been previously shown in various reports that typical ALD on TMDCs results in clusters formed on the surface rather than a uniform film, primarily because of the lack of surface dangling bonds on TMDCs. Ultraviolet-ozone (UV-O_3) functionalization of TMDCs has been found to be an effective route to producing more uniform ALD oxide films on TMDCs because it induces adsorbed oxygen on the surface (i.e., Se-O_{ads}) which serve as reaction sites for the ALD precursors on the otherwise unreactive surface. This functionalization for ALD has been well-replicated for MoS_2, but is less trivial for other TMDCs such as WSe_2. The main goal of this current work is to benchmark UV-O_3 functionalization of WSe_2 as a promising route towards achieving directly integrated sub-5 nm gate dielectrics. Various UV-O_3 exposure times will be tested on geological WSe_2 crystals. XPS will be performed after each UV-O_3 exposure to check for oxygen adsorption on the surface and/or oxidation of the WSe_2 constituents. To investigate how effective the surface functionalization is for ALD, AFM will be performed post-ALD of HfO_2 to study the morphology of the resultant layer. Using the best UV-O_3 processing parameters, various thicknesses (between 2-10 nm) of HfO_2 and Al_2O_3 will be deposited on functionalized WSe_2 substrates. Subsequent AFM characterization will be performed to analyze the resulting film morphology and uniformity. The downscaling thickness limit will be determined as the thinnest pinhole-free film produced. XPS will be performed on the HfO_2/WSe_2 and Al_2O_3/WSe_2 heterostructures to analyze their interface chemistry and band alignment.

Electronic Materials and Photonics Division
Room On Demand - Session EM-Invited On Demand

Electronic Materials and Photonics Invited On Demand Session

EM-Invited On Demand-1 Light Management Strategies for Photovoltaics: Luminescent Concentrators and Passive Cooling for Modules*, Vivian* ***Ferry,*** University of Minnesota, USA **INVITED**

The solar spectrum is a broad and diffuse light source, but solar panels operate most efficiently at wavelengths near the semiconductor bandgap and over a limited range of incident angles. This talk will discuss different strategies to manage the solar spectrum in photovoltaics: the first part will discuss luminescent solar concentrators that harvest diffuse, high energy sunlight and are integrated into architectural panels, where we use nanostructured luminescent materials and photonic surfaces to enhance performance. The second part will discuss optical strategies to reduce the operating temperature of photovoltaic modules.

Our work on luminescent solar concentrators uses two different nanocrystal luminophores, CdSe/CdS core-shell nanocrystals and Si nanocrystals, embedded into a polymer matrix. These light-emitting nanocrystals offer several advantages over dye molecules, but also exhibit detrimental scattering when aggregated. I will discuss the preparation of nanocrystal-polymer composites with high optical clarity for these applications. The CdSe/CdS nanocrystals are embedded into an alternative polymer, PCHE, and coated into very thin films on glass. The Si nanocrystals are incorporated into PMMA and deposited in thin films via blade coating, and we show that this method results in higher loading fractions than bulk composites. We then apply photonic structures to these luminophore-polymer composites that reduce optical losses and assist in guiding light efficiently toward the edge of the concentrator and onto a small-area solar cell.

The second part will discuss photonic structures for light management in photovoltaic modules. These structures are designed to provide both optical and thermal benefit: they act as broadband and omnidirectional antireflection coatings to improve incoupling of sunlight to the module, while simultaneously reflecting near-infrared light to keep the solar cell operating temperature low. We have developed models that predict energy yield improvement for particular locations, based on typical meteorological year data, and agree with experimental measurements on test modules. We use this model to predict and contrast the performance of mirrors on the outer glass, the surface of the cell, and the rear contact, showing that the mirrors on the glass offer the most temperature reduction. Mirrors on the cell surface, while attractive for reduced weathering, are limited by the textured surface of crystalline Si as well as the optical losses of the encapsulant. To circumvent the multiple reflections at the cell surface, we examine an alternative design consisting of idealized scatterers at the cell interface, and compare the performance of these nanostructures to idealized mirrors.

EM-Invited On Demand-7 Epitaxial Quantum Dots for Quantum Science and Technology*, **Sam Carter**, J. Grim, A. Bracker, M. Yakes, M. Zalalutdinov, C. Kim,* US Naval Research Laboratory*; M. Kim,* KeyW Corporation*; D. Gammon,* US Naval Research Laboratory **INVITED**

Self-assembled indium arsenide quantum dots are a promising platform for applications in quantum science and technology. This system has the advantages of a robust solid state host, strong optical transitions, mature device fabrication, tunable properties, and a scalable, monolithic architecture. Of particular importance for many applications is the ability to charge the dots with a single electron or hole in order to make use of a spin memory. We have integrated electrical diode structures within various optical cavities and mechanical resonators that allow charging of dots and control over spin. In photonic crystal cavities, this has enabled demonstrations of fast, optical spin rotations, cavity-stimulated Raman emission, and strong coupling [1,2]. In mechanical resonators this has enabled the demonstration of large spin-mechanical coupling with both hole spins and the singlet-triplet system in pairs of dots [3,4].

Quite recently we have also made significant progress in solving two important long-standing challenges with quantum dots. The first challenge is to combine in one system the ability to have both fast, optical control of spin and efficient spin readout, which we have addressed by using a set of higher energy optical transitions with one hole in an excited orbital. These transitions provide fast optical control while the lowest energy transitions give efficient spin readout. The second challenge is inhomogeneity of quantum dot emission energies, which we have addressed using a localized strain tuning technique that allows multiple dots within the same optical waveguide to be tuned into resonance. Using this technique we have demonstrated superradiance of three quantum dots embedded in a nanophotonic waveguide [5].

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EM-Invited On Demand-13 Van der Waals and remote epitaxy of complex materials*, **Jian Shi,*** Rensselaer Polytechnic Institute **INVITED**

Dimensionality effect has been found interesting in exploring new physics and effective in engineering materials' physical properties. However, often intrinsic material behaviors are clouded by the underlying support through strongly-coupled interface. In this talk, I will show our efforts and discovery on developing weakly-coupled epitaxial interface for semiconducting halides. I will present the serendipity and challenges while working on complex oxide interfaces.

EM-Invited On Demand-19 Functional Oxide Materials for Silicon Photovoltaics*, **Kristopher Davis,*** University of Central Florida **INVITED**

The incredible cost reductions realized by the photovoltaics (PV) industry have been, and continue to be, driven by a combination of technology improvements and manufacturing scale. A primary example of such a technological enhancement is the development of Al_2O_3 surface passivation using atomic layer deposition (ALD). The low recombination achieved with thin Al_2O_3 films on crystalline silicon (c-Si) surfaces, coupled with the industry's ability to produce high throughput spatial ALD and later, plasma enhanced chemical vapor deposition (PECVD) tools, ushered in the large scale transition from the Al back surface field (Al-BSF) cell architecture to passivated emitter and rear cells (PERC). Alternative c-Si cell architectures, like a-Si:H/c-Si heterojunctions (SHJ) and interdigitated back contact (IBC) cells, offer higher cell efficiencies, but the manufacturing cost and complexity have limited their market share compared to PERC. An ideal solar cell should feature fully passivated surfaces with carrier-selective layers that: (1) minimize minority carrier concentrations at the absorber surface; (2) maximize majority carrier transport; and (3) minimize parasitic optical absorption. Achieving these criteria with a simple cell architecture and minimal processing steps in a high-volume manufacturing environment is a key challenge. Wide bandgap oxide materials possess a rich diversity in electronic band structure and versatility in synthesis and doping. They have emerged as promising candidates with the ability to provide photon management, surface passivation, carrier selectivity, and lateral carrier transport. This presentation will provide an up to date assessment of the potential for functional oxides in silicon photovoltaics.

EM-Invited On Demand-25 Building MOFs from the Gas Phase at the Molecular Level - Active Surfaces by Combining Organics with Inorganics*, Ola Nilsen,* University of Oslo, Norway **INVITED**

The MLD technique could be considered as the ultimate in additive manufacturing where it builds materials one molecular layer at the time from the gas phase. The current presentation will focus on growth of such materials with emphasis on building units containing carboxylic acids. Inorganic carboxylates are mostly stable, offering high saturation of the metal centre's coordination sphere, leading up to the plethora of such structures as metalorganic frameworks (MOF). Such materials can be grown via the gas phase, and examples from growth of the UiO-66 series with variations in linker length and complexity will be given, in addition to alternative systems. This introduces concepts such as modulation of growth, reservoir effects, tuning of chemical reactivity, and amorphous porosity. The current contribution will provide highlights from such growth of organic- inorganic hybrid materials including MOF materials.

EM-Invited On Demand-31 2020 AVS Peter Mark Memorial Award Lecture: Efficient Graphene Hot Electron Devices: Electrochemistry and Electron Emission*, Rehan Kapadia*[1]*,* University of Southern California **INVITED**

In this talk, we will discuss recent work in hot electron devices, focusing on how graphene enables efficient hot electron devices that go beyond the present state of the art in both electron emission and electrochemistry.

First, we show that the onset of electrochemical and photoelectrochemical reactions on a graphene surface can be modified with a semiconductor-insulator-graphene (SIG) device due to injection of hot-electrons from the silicon to the graphene. We observe that the device functions similar to a catalyst, but modifies electrochemical behavior through purely electronic signals. Unlike a material catalyst, such as platinum, which reduces the overpotential at a given current by modifying the transition state energy, the electronic catalyst explored here tunes the onset potential of the reaction by modifying the energy of photoelectrons with respect to the electrochemical reduction energy levels. As a model systems, the hydrogen evolution reaction on graphene is shown to be modified in an n-Si/Al_2O_3/graphene electrochemical device, and a p-Si/Al_2O_3/graphene photoelectrochemical device. Uniquely, it is shown that for every volt of bias applied across the silicon-insulator-graphene junction, the onset of hydrogen reduction on the graphene surface is modified by 1.45 V with a saturation photocurrent density of ~40 mA/cm^2 indicating nearly ideal minority carrier collection despite the insulator layer.

Next, we show how hot-electron processes can dramatically reduce the optical power densities required for photoemission. In metallic emitters, single-photon, multi-photon, or strong-field emission processes are the three mechanisms via which photoemission takes place. Photons with energy lower than the material workfunction can only drive photoemission through the multi-photon, or strong-field processes, both of which require large optical powers, limiting the integration of photoemitters with photonic integrated circuits. Here, we show that a waveguide integrated graphene electron emitter excited with 3.06 eV photons from a continuous wave (CW) laser exhibits two hot-electron processes that drive photoemission at peak powers >5 orders of magnitude lower than previously reported multi-photon and strong-field metallic photoemitters. Optical power dependent studies combined with modeling illustrate that the observed behavior can be explained by considering direct emission of excited electrons. These processes are dramatically enhanced in graphene due to the relatively weak electron-phonon coupling and the single layer structure. These results show that hot electron devices still offer a rich area of exploration.

Exhibitor Technology Spotlight Workshops
Room On Demand - Session EW-On Demand
Exhibitor Technology Spotlight Contributed On Demand

EW-On Demand-1 New Developments for Surface Analysis from Thermo Fisher Scientific*, Tim Nunney,* *P. Mack, R. Simpson, H. Tseng,* Thermo Fisher Scientific, UK*; J. Lallo,* Thermo Fisher Scientific

In this presentation we will showcase the latest developments in surface analysis and materials analysis instrumentation from Thermo Fisher Scientific.

Fundamental Discoveries in Heterogeneous Catalysis Focus Topic
Room On Demand - Session HC-Contributed On Demand
Fundamental Discoveries in Heterogenous Catalysis Contributed On Demand Session

HC-Contributed On Demand-1 Operando Structural Characterization of Co-Promoted MoS_2 Nanoparticles Under Hydrodesulfurization Reaction Conditions Using the Reactor STM*, Mahesh Krishna Prabhu,* Leiden University, The Netherlands*; I. Groot,* Leiden University, Netherlands

Hydroprocessing plays a key role in reducing global SOx and NOx emissions in order to abate the global warming and the associated climate change. Understanding and improving the widely used Co-promoted MoS_2 catalysts for hydrodesulfurization (HDS) is an important step in this direction. In this presentation, operando structural characterization of Co-promoted MoS_2 nanoparticles at semi-industrial reaction conditions will be presented. ReactorSTM[1,2] has been used to obtain atom-resolved images of Co-promoted MoS_2 and closely associated phases such as CoS_2 under a gas mixture of hydrogen and methanethiol at industrially relevant conditions. Ex-situ XPS characterization has been performed to investigate the chemical changes occurring on the catalyst surface. Additionally, candidate atomic models to explain the STM images have been proposed. The results of this study provide valuable insights into the HDS activity of Co-promoted MoS_2 nanoparticles.

[1] Review of Scientific Instruments 85, 083703 (2014);[2] Nature communications volume 10, 2546 (2019)

HC-Contributed On Demand-4 Understanding Ligand-Directed Heterogeneous Catalysis: When the Dynamically Changing Nature of the Ligand Layer Controls the Hydrogenation Selectivity*, Swetlana Schauermann,* *C. Schroeder, M. Schmidt,* Kiel University, Germany

Selectivity of multi-pathway surface reactions depends on subtle differences in the activation barriers of competing reactive processes, which is difficult to control. One of the most promising strategies to overcome this problem is to introduce a specific selective interaction between the reactant and the catalytically active site, directing the chemical transformations towards the desired route. This interaction can be imposed via functionalization of a solid catalyst with ligands, promoting the desired pathway via steric constrain and/or electronic effects. The microscopic-level understanding of the underlying surface processes is an important prerequisite for rational design of this new class of ligand-functionalized catalytic materials.

In this contribution, we present a mechanistic study on formation and dynamic changes of a ligand-based heterogeneous Pd catalyst for chemoselective hydrogenation of a,b-unsaturated aldehyde acrolein. Deposition of allyl cyanide as a precursor of a ligand layer renders Pd highly active and nearly 100 % selective toward propenol formation by promoting acrolein adsorption in a desired configuration via the C=O end. Employing a combination of real space microscopic (STM) and *in operando* spectroscopic (IRAS) surface sensitive techniques, we show that an ordered active ligand layer is formed under operational conditions, consisting of stable butylimin species. In a competing process, unstable amine species evolve on the surface, which desorb in the course of the reaction. Obtained atomistic-level insights into the formation and dynamic evolution of the active ligand layer under operational conditions provide important input

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[1] **AVS 2020 Peter Mark Awardee**

required for controlling chemoselectivity by purposeful surface functionalization.

HC-Contributed On Demand-7 Derivatization Effect of Cobalt Phthalocyanine on the Catalytic Activity for Carbon Monoxide Reduction*, **Yutaro Umejima**, J. Nakamura,* The University of Electro-Communications (UEC-Tokyo), Japan

The electrochemical conversion of carbon monoxide (CO) has attracted attention for its use in renewable energy sources. In general, noble metals have been commonly used as effective catalysts for the carbon monoxide reduction (COR) reactions. However, noble metals have many problems including high overpotential and high cost. Therefore, noble-metal-free catalysts with high COR reaction activity are required. Recently, cobalt phthalocyanine (CoPc) has been confirmed to exhibit a high activity in the COR reaction [1].On the other hand, it has been found that the catalytic activity of the iron phthalocyanine (FePc) molecule for oxygen reduction reaction (ORR) is significantly improved by its derivatization [2].

In this study, we elucidate the change in catalytic activity with derivatization of CoPc for the reduction process of CO using first-principles calculations. The catalytic activity for the COR reactions was evaluated using the computational hydrogen electrode model proposed by Nørskov *et al*. [3] For derivative molecules of CoPc, we considered CoAzPc-4N and CoAzPc-8N. It has been confirmed that such an introduction of N to Pc results in the catalytic activity improvement for ORR [2]. The CoAzPc-4N and CoAzPc-8N molecules have four pyridine and pyrimidine rings, respectively, instead of the four benzene rings of CoPc. In order to evaluate catalytic activities of CoPc and its derivatives for COR reaction, we calculated free energies for various intermediates. Methane and methanol were assumed as final products.

It has been confirmed that (1) the reaction proceeds as $CO \rightarrow {}^*CO \rightarrow {}^*CHO \rightarrow {}^*CHOH \rightarrow {}^*CH_2OH \rightarrow CH_3OH$, (2) methanol is the most stable final product, and (3) the reaction determining step is $^*CHO \rightarrow {}^*CHOH$ for CoPc and its derivatives. The overpotentials of CoPc, CoAzPc-4N, and CoAzPc-8N at the reaction determining step are estimated to be 1.21 V, 1.18 V, and 1.14 V, respectively; such derivatization of CoPc improves the catalytic activity of the COR reaction as well as the ORR of FePc. It has been concluded that the substitution by the electron-withdrawing species leads to the higher catalytic activity of CoPc for the COR reaction.

References

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[3] J. K. Nørskov, J. Rossmeisl, A. Logadottir, L. Lindqvist, J. Phys. Chem. B **108**, 17886 (2004)

HC-Contributed On Demand-10 Surface Characterization and Methane Activation of $SnO_x/Cu_2O/Cu(111)$ Inverse Model Catalysts*, **Jindong Kang**,* Stony Brook University*; J. Rodriguez ,* Brookhaven National Laboratory

Many efforts have been devoted to efficiently utilize methane, the primary component of abundant low-cost natural gas and a major contributor to global warming. Therefore, the conversion of methane to other value-added chemicals has been one of the intensive studies in catalysis in the past several decades. The key to converting methane to such chemicals is to activate highly stable C-H bonds in methane and control the first C-H bond dissociation known as the rate limiting step in the direct methane conversion process. The aim of this project is to develop an efficient catalyst which can reduce the energy barrier for the first C-H bond dissociation and activate methane at low temperatures. Herein, we introduce a novel $SnO_x/Cu_2O/Cu(111)$ inverse model catalyst. The surface structure and the chemical state of SnO_x nanoclusters on $Cu_2O/Cu(111)$ were investigated by Scanning Tunneling Microscopy (STM) and Ambient Pressure X-ray Photoemission Spectroscopy (AP-XPS). Our results show that this novel catalyst activates methane at low temperature and will provide new guidance to design new efficient catalysts for the methane conversion.

HC-Contributed On Demand-13 Crystal Plane Effect of Cu_2O Clusters on the Catalytic Performance of Pt/Cu_2O under CO Oxidation*, **Seunghwa Hong**, H. Choi, D. Kim, J. Park,* Korea Advanced Institute of Science and Technology (KAIST) & Institute for Basic Science (IBS), Korea (Republic of)

Metal nanoparticle supported on metal oxide is the most widely used heterogeneous catalyst. In supported metal catalyst, the interface between metal and support modify their coordination and electronic structure due to strong metal-support interaction (SMSI) which result in altering catalytic performance. Thus, controlling the interface of metal and support is a key strategy for enhancing catalytic activity. However, a fundamental understanding of SMSI is not fully unveiled due to difficulties in characterization in actual catalytic reaction conditions. Herein, using Cu_2O nanocubes and octahedral clusters as model catalysts, we investigated the catalytic performances of Pt/Cu_2O by using ambient pressure X-ray photoelectron spectroscopy (AP-XPS) and diffuse reflectance FT-IR spectroscopy (DRIFT) as in-situ characterization technique. The catalytic measurement as well as in-situ surface characterization results indicates that the facet-dependent interfacial site affects the catalytic activity of CO oxidation significantly, implying the tunability of the catalytic activity by controlling the crystal plane of Cu_2O.

HC-Contributed On Demand-16 Catalytic Synergy on PtNi Bimetal Catalysts Driven by Interfacial Intermediate Structure*, **Taek-Seung Kim**,* Korea Advanced Institute of Science and Technology (KAIST) & Institute for Basic Science (IBS), Korea (Republic of)*; J. Kim,* Institute for Basic Science (IBS), Korea (Republic of)*; H. Song, D. Kim, J. Park,* Korea Advanced Institute of Science and Technology (KAIST) & Institute for Basic Science (IBS), Korea (Republic of)

Platinum–based bimetallic catalysts exhibit surface atomic rearrangement at various adsorbate environments, which significantly impacts catalysis. A molecular-level understanding of intermediate structures on model catalysts including single crystal and nanoparticle surfaces under reaction conditions is essential for developing novel, high-performance bimetal catalysts. By using *operando* surface techniques on PtNi single crystal and nanoparticles, we address the issue of bridging pressure/materials gap in the molecular mechanism of bimetallic synergy effect. We show that intermediate $Pt\text{-}NiO_{1\text{-}x}$ interfacial structures drive the catalytic synergistic effect observed on both single crystal Pt_3Ni (111) surface and Pt_3Ni nanocrystals. *Operando* surface techniques, including ambient pressure scanning tunneling microscopy and X-ray photoelectron spectroscopy (AP-XPS), were used to probe the $Pt\text{-}NiO_{1\text{-}x}$ interfacial structures on Pt_3Ni (111). The DFT calculation confirms the role of intermediate structure which boosts the catalytic activity of CO oxidation. For further understanding of the bimetallic synergy in the Pt_3Ni nanocrystal, we utilized environmental transmission electron microscopy, and operando spectroscopies including AP-XPS and diffuse reflectance infrared Fourier-transform spectroscopy. Real-time microscopic observation at ambient pressure shows the formation of oxygen-driven Ni oxides clusters on the surface and direct evidence of $Pt\text{-}NiO_{1\text{-}x}$ interfacial structure formation. Spectroscopic analysis and catalytic measurements elucidate the role of $Pt\text{-}NiO_{1\text{-}x}$ interfacial structures and the catalytic reaction mechanism for CO oxidation. Our results indicate that oxide-metal interfacial intermediate structures is directly related to the enhancement of the catalytic activity, and strong metal-support interaction effect observed in mixed catalysts.

HC-Contributed On Demand-19 Reactivity of Butanol on $TiO_2/Au(111)$ Inverse Model Catalysts*, **Lyssa Garber**, A. Galgano, C. Rogers, 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 making it an attractive alternative fuel. To better understand how butanol breaks down in heterogeneous catalytic processes, temperature programmed desorption (TPD) is used to investigate its reaction on $TiO_2/Au(111)$. Inverse model catalysts of interest were formed by depositing TiO_2 nanoparticles onto Au(111) using physical vapor deposition. Low temperature desorption features help to understand how the molecule adorbs to the surface while the high temperature peaks are used to understand chemical reactivity and selectivity. Low temperature peaks indicate different molecular packing of 1- and 2-butanol. The major high temperature products from the reaction of 2-butanol on $TiO_2/Au(111)$ are 2-butanone and butene, observed at ~500 K. The selectivity of the reaction was not altered during successive desorption experiments, indicating that the model catalyst was stable without reoxidation between experiments. Preliminary studies of the reaction of 1-butanol indicate that both reduced and oxidized products are formed, but need to be further studied to identify the species and stability. Atomic force microscopy (AFM) images show that the inverse model catalyst has ~0.16 ML of TiO_2 dispersed across the Au(111) surface in predominantly 1D nanoparticles. Early studies of butanol on $TiO_2/Au(111)$ suggest that the structure affects the reactivity and stability of butanol at high temperatures.

HC-Contributed On Demand-22 Surface-Dependent Selectivity of Ethanol With TiO_2 Modified Au(111) Model Catalysts*, **Clayton Rogers**, D. Boyle, M. DePonte, A. Baber,* James Madison University

The dehydrogenation of small primary alcohols is widely used to produce H_2 and aldehydes to be used as feedstock chemicals for further manufacturing processes. While wet dehydrogenation is used in industry, it is wasteful and complicates the separation process for the desired products. The use of reducible oxides provides an easily regenerated source of oxygen on Au(111) for the reaction of ethanol. Depending on the surface preparation conditions, Au(111) supported TiO_2 nanoparticles react with small alcohols to form either oxidization or elimination products. In this work, we investigate the role of surface modifications on the selective oxidation of ethanol to acetaldehyde over the elimination reaction to form ethylene and water. A systematic study of ethanol reactivity over several TiO_2/Au(111) surfaces elucidates the effect of surface conditions on the selectivity of the reaction between ethanol and TiO_2/Au(111). The reactivity of the surface for ethanol oxidation was altered by controlling the oxidation state of TiO_x (x<2) and coverage of TiO_2. Atomic force microscopy (AFM) was used to study the structure of the Au(111) supported TiO_2 nanoparticles and ultrahigh vacuum temperature programmed desorption (TPD) was used to monitor the selectivity of the reaction between ethanol and TiO_2/Au(111). Low coverages of fully oxidized TiO_2 nanoparticles on Au(111) are active for the selective oxidation of ethanol to form acetaldehyde, and subsequent experiments indicate that selectivity is not affected, even without reoxidation treatments.

HC-Contributed On Demand-25 Active Sites and Structural Transformation of $NiFeO_x$ Catalysts during Electrocatalytic Oxygen Evolution Reaction: Effects of Catalyst Loading and Support*, **Xingyi Deng**, D. Kauffman, D. Sorescu,* National Energy Technology Laboratory

Particle size, catalyst support, and in situ structural transformation can all impact the electrocatalytic activity of metal and oxide catalysts. Here we used a combination of ultrahigh vacuum catalyst synthesis, surface science characterizations including scanning tunneling microscopy (STM) and X-ray photoelectron spectroscopy (XPS), electrochemical measurements, and density functional theory (DFT) modeling to study the electrocatalytic oxygen evolution reaction (OER) at $NiFeO_x$ catalysts deposited on Au(111) and highly oriented pyrolytic graphite (HOPG) electrodes. The formation of well-defined catalysts with precise loadings and atomic compositions allowed us to accurately track their composition and loading dependent electrocatalytic activity, monitor structural transformations that occurred during OER, and create realistic computational models. DFT calculations predicted Fe atoms residing at the edges of $NiFeO_x$ catalysts to be the most favorable OER reaction site, and soft X-ray absorption spectroscopy data suggested a higher population of undercoordinated Fe sites in small, as-synthesized $NiFeO_x$ catalyst particles. However, Au(111) substrates with low catalyst loadings experienced severe surface restructuring during OER that inhibited the activity of very small $NiFeO_x$ particles. At sufficiently high catalyst coverage the Au surface restructuring was suppressed and the $NiFeO_x$ catalysts transformed from their initial structure into an aggregated collection of smaller nanoparticles. The dual effects of Au surface restructuring and catalysts transformation created an unexpected loading-dependent activity trend for Au-supported catalysts. The detrimental impacts of surface restructuring were not found with HOPG substrates, and HOPG-supported $NiFeO_x$ catalysts demonstrated a more expected loading-dependent activity trend. Our study reveals some key fundamental insights into the $NiFeO_x$ catalyst system and points to the importance of catalyst transformations and substrate choice for understanding and optimizing OER performance.

HC-Contributed On Demand-28 Activation of O_2 on CeO_2 Nanoparticle Surfaces by Electron Transfer*, M. Brites Helú,* Instituto para el Desarrollo Tecnológico de la Industria Química INTEC (CONICET-UNL), Argentina*; A. Norton,* Department of Chemical Engineering, University of Delaware*; S. Collins,* Instituto para el Desarrollo Tecnológico de la Industria Química INTEC (CONICET-UNL), Argentina*; D. Stacchiola, J. Boscoboinik,* Center for Functional Nanomaterials, Brookhaven National Laboratory*; **Florencia Calaza**,* Instituto para el Desarrollo Tecnológico de la Industria Química INTEC (CONICET-UNL), Argentina

It is well known that VOCs being recognized as major responsible for the increase in global air pollution. Catalytic combustion is an efficient technology for the abatement of VOC, which are oxidized over a catalyst at temperatures much lower than those of the thermal process. Specifically, gold supported catalysts on CeO have shown a great performance in the oxidation of CO, methanol, toluene, etc. Besides, it is important to clarify the role of the support in such reaction. Ceria has the key property of high oxygen storage capacity which originates in its ability to rapidly switch from Ce^{+3} to Ce^{+4} oxidation states as the environment changes from reducing to oxidizing and vice versa. Its redox behaviour is influenced by the substituent lattice groups that could be incorporated during different catalyst pretreatments and could affect the oxidation of VOC. This could be understood as the influence of oxygen vacancies and/or **absorbed** or coadsorbed H on the activation of oxygen molecules. The latter leads to the formation of superoxide and peroxide molecules on the surface, which could in principle be highly reactive towards oxidation of organic molecules.

In this context, we study, by IR spectroscopy (DRIFTS) and mass spectrometry (MS), the interaction of O_2 with the modified CeO_2 based material, by creating vacancies following different treatments in reducing environments. The possible role of the vacancies and/or presence of H atoms in the electron transfer from the surface to the oxygen molecule is discussed. Using AP-XPS we are able to prove that the surface/near surface of CeOx presents a charging effect which could be due to accumulated charge/electrons which then transfer to O_2. Preliminary results showing reactivity of these activated molecular oxygen species (super- and peroxides) are presented regarding the catalytic oxidation of CO.

HC-Contributed On Demand-31 Comparison of Single Rh Adatoms on A-Fe_2O_3(1-102) and TiO_2(110) Stabilized by Adsorbed Water*, **Lena Haager**, F. Kraushofer,* TU Wien, Austria*; M. Eder,* TU München, Germany*; A. Rafsanjani-Abbasi, G. Franceschi, M. Riva, P. Sombut, M. Atzmueller, M. Schmid,* TU Wien, Austria*; C. Franchini,* Universitá di Bologna, Italy*; U. Diebold, G. Parkinson,* TU Wien, Austria

Despite its high cost, rhodium is a widely applied catalyst primarily used in nanoparticle form for converting toxic gases in automobiles. It is also utilized in organometallic complexes, such as the Wilkinson catalyst, for the hydrogenation of olefins and for converting alkenes to aldehydes through a process known as hydroformylation. So-called “single-atom” catalysis offers an opportunity to reduce the amount of Rh required for traditional heterogeneous catalysis, and a path to heterogenize homogeneous reactions, with the advantage of easy separation of catalyst and product.

Using scanning tunneling microscopy (STM), non-contact atomic force microscopy (nc-AFM) and x-ray photoemission spectroscopy (XPS) we compare the stability of Rh adatoms on two different model supports: α-Fe_2O_3(1-102) and TiO_2(110), both after metal deposition in UHV and in a 2×10^{-8} mbar water background. We show that the Rh adatoms on α-Fe_2O_3(1-102) sinter in UHV but are stabilized by water up to 150 °C through coordination to 2 – 3 OH ligands. In contrast, Rh adatoms on TiO_2(110) could not be stabilized above room temperature in either environment.

HC-Contributed On Demand-34 Polarons in Single Atom Catalysts: Case Study of Me_1=[Au_1, Pt_1, Rh_1] on TiO_2(110)*, **Panukorn Sombut**, L. Haager, M. Atzmueller, Z. Jakub,* TU Wien, Austria*; M. Reticcioli,* University of Vienna, Austria*; M. Meier, G. Parkinson,* TU Wien, Austria*; C. Franchini,* University of Vienna, Austria

Identification of the exact local environment of a single-atom catalysts (SAC) on metal oxide surfaces is crucial for understanding the reactivity as well as the catalytic properties of such systems. On TiO_2(110), the stability and reactivity of adsorbed adatoms is further complicated by the presence of oxygen vacancies and associated polaron charge, as both can affect the energetic, electronic configuration and local geometry of adsorbed adatoms. In this work the adsorption of group 9 to 11 transition metal adatoms (Rh, Pt and Au) are computationally studied by means of density functional theory (DFT, plus on-site Hubbard U), and compared with results obtained by experimental surface techniques such as scanning tunneling microscopy (STM), for Rh_1, and with available literature (Au_1 and Pt_1). Despite the many works on this subject, it is still unclear why Au and Pt are experimentally observed to adsorb in the O vacancy, contrary to Rh. By investigating the most stable adsorption site, oxidation state and intermingled interaction among adatoms, O vacancies and polarons our data attempt to decipher the physical and chemical origin of the observed trend and to provide a conclusive interpretation of the puzzling observation.

HC-Contributed On Demand-37 Conformer-Selective Adsorption of 1-Propanol on Ag(111) from Theoretical Analysis of Experimental Reflection Absorption Infrared Spectra*, **Ravi Ranjan**, M. Trenary,* University of Illinois at Chicago

The experimental reflection absorption infrared spectrum of 1-propanol at 180 K is remarkably simple with usually sharp peaks with FWHM (full-width half maxima) of 1.1, 2.1, 1.6, and 4.0 cm^{-1} for the peaks at 1015, 1051, 1455, and 2948 cm^{-1}, respectively. This suggests that 1-propanol adsorbs as a single conformer, despite the fact that five different conformers of nearly the same energy are known for the gas-phase molecule. The stability of the different 1-propanol conformers on Ag(111) was investigated with DFT using a hybrid density functional (B3LYP) with additional empirical dispersion corrections (B3LYP-D3) using a Ag$_{19}$ cluster model of the Ag(111) surface. The five conformers (Gg, Gg', Gt, Tg, Tt) are named with a two-letter code. The first letter (G for gauche, T for trans) corresponds to the structure relative to the C-C-C-O dihedral angle, and the second letter (g for gauche, t for trans) refers to the C-C-O-H dihedral angle. In the gas phase, full geometry optimization gives zero-point corrected relative energies of 0.0, 0.06, 0.08, 0.21, and 0.28 kcal/mol respectively for Tt, Tg, Gt, Gg, and Gg' conformers at the B3LYP/6311++G(2d,2p) level. The global minimum of 1-propanol at this level is for the Tt conformer. On the silver cluster at the B3LYP-D3/6-311++G(2d,2p) level, the adsorption energies with dispersion correction are 17.84, 17.41, 17.01, 16.86, and 16.84 kcal/mol, respectively for Tt, Gg', Tg, Gg, and Gt conformers. The Tt conformer is the most stable conformer at this level of theory.The theoretical infrared spectra of all conformers are compared to the experimental spectrum. The calculated Tt spectrum best matches the experimental spectrum at 180 K. This reveals that adsorption on the Ag(111) preferentially stabilizes only one of the five possible conformers.

HC-Contributed On Demand-40 Ambient-Pressure CO Driven Restructuring of Cu(111) by Reflection Absorption Infrared Spectroscopy*, Arephin Islam,* University of Illinois at Chicago*; C. Kruppe ,* Intel Corporation*; M. Trenary,* University of Illinois at Chicago

Recently, restructuring of surfaces that occur under applicable operating conditions has aroused great interest. The structural changes have been correlated with changes in selectivity and linked to bond scission in heterogeneous catalysis. Metal single-crystals make excellent model systems to study restructuring by adsorbates since they are well defined and can be atomically prepared in ultra-high vacuum. The most popular adsorbates that cause well-defined surface restructuring are atomic oxygen and carbon monoxide. Restructuring due to CO has been seen on Cu(111) before[1], and CO is known to induce segregation in bimetallic materials. Furthermore, CO plays multiple roles including reactant, poison, product, or additive in catalytic processes such as CO hydrogenation, CO oxidation, methanol synthesis, and the water gas-shift (WGS) reaction. We have used reflection absorption infrared spectroscopy (RAIRS) to study the ability of CO to restructure Cu(111) and its subsequent impact on reactivity in the WGS reaction under ambient conditions. With polarized infrared radiation, the gas phase and surface species are easily distinguished. In the presence of ambient pressures of CO at 300 K, peaks at 1800-2100 cm^{-1} were readily observed and the spectral changes were monitored for different time intervals. The results demonstrate that the Cu surfaces have restructured, and new CO binding sites were created. Upon evacuation of the high-pressure CO, a new peak related to strongly bound CO at 2005-2023 cm^{-1} is reported that remains on the surface in UHV at room temperature.

References

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HC-Contributed On Demand-43 Metal Vapor Adsorption Calorimetry on Clean Surfaces of Oxide and Mixed-Oxide Single Crystals and Powdered Catalyst Support Materials*, Charles T. Campbell,* *Z. Mao, W. Zhang,* University of Washington, Seattle

Many important catalysts and electrocatalysts for energy and environmental technologies involve late transition metal atoms and nanoparticles dispersed across the surface of some powdered oxide support material.The long-term stability of these materials depends strongly on the strength of bonding of the metal atom and nanoparticles to the support surface. This talk will review recent studies were we have measured these bond strengths to clean and well-defined surfaces using metal vapor adsorption calorimetry.This includes planar single crystal surfaces, as well as the clean surfaces of high-surface-area powdered support materials of the type used industrially. Specifically, we measured the heat of adsorption versus coverage of Ni on MgO(100) and CeO$_2$(111) surfaces, from which we extracted the adhesion energy (E_{adh}) at these Ni/oxide interfaces. The results proved the predictive ability of our earlier linear correlation of E_{adh} with metal oxophilicity based on earlier measurements with metals that are less oxophilic than Ni. We also describe measurements of the adsorption energies of Ag atoms and the adhesion energies of Ag nanoparticles to drop-cast powders of anatase TiO$_2$ and to the (001) surface of calcium niobate nanosheets deposited in thin films by Langmuir-Blodgett (LB) techniques. This second application shows that LB deposition of multilayer films of such perovskite nanosheets, followed by their annealing in ultrahigh vacuum, provides a powerful new approach for studying surface of mixed oxides that are as clean and well-ordered as typical surfaces of single crystal oxides studied in surface science. The new calorimeter used for the study of these high-area support materials offers the potential for rapid screening of technical support materials for the strength with which they bond metal atoms and nanoparticles, which may aid in discovering better catalyst support materials.

Work supported by DOE-OBES Chemical Sciences Division.

HC-Contributed On Demand-46 Sum Is Better Than the Parts: CrCoFeNi High Entropy Alloy as Hydrogen Evolution Catalyst in Acidic Solution*, Frank McKay,* Louisiana State University*; Y. Fang,* Louisiana State Universityt*; O. Kizilkaya,* Louisiana State University*; P. Singh,* Ames Laboratory*; D. Johnson,* Iowa State University*; A. Roy, D. Young, P. Sprunger, J. Flake, W. Shelton, Y. Xu,* Louisiana State University

Pt plays a central role in industrial and technological catalytic applications, but limitations on sourcing and availability make reliance on it a potential weakness of modern economies. Alloying base metals with Pt has long been practiced to enhance catalytic performance and reduce use of Pt. Alloys of 3d base metals, e.g. Cr, Fe, Co, and Ni, with Pt have been extensively studied as electrocatalysts for reactions including oxygen reduction. Here we report that a random, equimolar alloy (or high entropy alloy, HEA) of the four base metals, being entirely free of Pt, can catalyze the electrochemical hydrogen evolution reaction in 0.5 M H2SO4 with an overpotential that is ca. 60 mV more than Pt at 1 mA/cm2 that is smaller than any of the component metals. While the HEA is not immune to dissolution, its activity remains stable with respect to repeated cycling up to 1000 times. DFT calculations based on a Super-Cell Random Approximates model of the HEA predict its surface to be partially oxidized under the given conditions, and the un-oxidized sites to adsorb atomic hydrogen with an average strength that is closer to that on Pt than on all the component metals. Hydrogen adsorption is further investigated via HREELS and compared with calculations. Changes in the surface and near-surface composition of the HEA are probed with XPS through increasing exposure to oxygen at room temperature. The results show that the elements preferentially oxidize in the order of Cr >> Fe > Co, with nearly no Ni oxidation up to 1,000 L of O2. Moreover, angle-dependent XPS and UPS measurements show that oxygen forms a passive surface layer, but the elemental metal concentration remains unchanged upon oxidation. Our findings provide tantalizing evidence for the potential of HEAs for chemical and catalytic applications.

HC-Contributed On Demand-49 The Influence of Palladium on the Hydrogenation of Acetylene on Ag(111)*, David Molina,* *M. Muir, M. Abdel-Rahman, M. Trenary,* University of Illinois - Chicago

We have used reflection absorption infrared spectroscopy (RAIRS) and temperature programmed reaction (TPR) to study the selective hydrogenation of acetylene on both a clean Ag(111) surface and on a Pd/Ag(111) single-atom-alloy surface. The partial hydrogenation of acetylene to ethylene is an important catalytic process that is often carried out using PdAg alloys. It is challenging to study the reaction with ultrahigh vacuum techniques because H_2 does not dissociate on Ag(111) and while H_2 will dissociate at Pd sites, H-atom spillover from Pd to Ag sites does not generally occur. We bypassed the H_2 dissociation step by exposing the surfaces to atomic hydrogen generated by the hot filament of an ion gauge. We find that hydrogen atoms react with acetylene to produce adsorbed ethylene at 85 K, the lowest temperature studied. This is revealed by the appearance of a RAIRS peak at 950 cm^{-1} due to the out-of-plane wagging mode of adsorbed ethylene when acetylene is exposed to a surface on which H atoms are pre-adsorbed. The formation of both ethylene and ethane are detected with TPR, but no acetylene coupling products, such as benzene, were found. From quantitative analysis of the TPR results, the percent conversion and selectivities to ethylene and ethane were determined. Low coverages of Pd enhance the conversion but do so mainly by increasing ethane formation.

HC-Contributed On Demand-52 In Situ Investigation of the Oxidation of Cu(111) and Reduction of Cu_2O Doped with Single Pt Atoms

A. Schilling, Tufts University*; K. Groden,* Washington State University*; J. Simonovis, A. Hunt,* Brookhaven National Laboratory*; R. Hannagan, V. Cinar,* Tufts University*; J. McEwen,* Washington State University*; E. Sykes,* Tufts University*;* ***Iradwikanari Waluyo,*** Brookhaven National Laboratory

The redox behavior of metal oxides, either as catalyst supports or as the active sites themselves, plays an important role in heterogeneous catalytic reactions. In many cases, the redox behavior of a metal oxide can be significantly affected by the presence of a dopant atom due to the introduction of additional active sites as well as new interfaces. In this talk, I will present recent results from the IOS (23-ID-2) beamline at the National Synchrotron Light Source II (NSLS-II) at Brookhaven National Laboratory, in which we used ambient pressure X-ray photoelectron spectroscopy (AP-XPS) to study the oxidation and reduction behavior of Cu(111) doped by single Pt atoms on the surface, initially forming a PtCu single-atom alloy. Complementary data from temperature-programmed desorption (TPD) experiments and results from density functional theory (DFT) calculations will also be presented. By probing the Pt 4f core level, we were able to clearly distinguish Pt atoms in different chemical and physical environments as well as monitor their evolution under oxidizing and reducing environments. XPS revealed that a mild oxidizing condition ($5x10^{-6}$ Torr O_2 at 400 K) can result in the formation of a complete Cu_2O thin film on the surface of the sample that covers the Pt atoms. TPD results show that the oxidized Pt/Cu_2O surface is inert and the Pt atoms are inactive in H_2 dissociation. AP-XPS was used to monitor the evolution of the oxide O 1s peak in 1 Torr H_2 at room temperature, which revealed that the presence of a small amount of Pt, at the single atom limit, significantly accelerates the reduction of Cu_2O by H_2, even when the Pt atoms are covered by an oxide layer. DFT calculations show that the presence of Pt atoms under the oxide layer weakens the Cu-O bonds in its immediate vicinity. This work highlights the role of the metal-oxide interface in heterogeneous catalysis in terms of its ability to influence the catalyst's ability to maintain a reduced state during a reaction.

HC-Contributed On Demand-55 Kinetics of the Thermal Oxidation of Ir(100) toward IrO2 Studied by Ambient-Pressure X–ray Photoelectron Spectroscopy

Zbynek Novotny, University of of Zürich & Paul Scherrer Institute, Switzerland*; B. Tobler,* University of Zürich, Switzerland*; L. Artiglia,* Paul Scherrer Institut, Switzerland*; M. Fischer, M. Schreck,* Universität Augsburg, Germany*; J. Raabe,* Paul Scherrer Institut, Switzerland*; J. Osterwalder,* Universität Zürich, Switzerland

Using time-lapsed ambient-pressure X-ray photoelectron spectroscopy, we investigate the thermal oxidation of single-crystalline Ir(100) films toward rutile IrO_2(110) in situ [1]. We initially observe the formation of a carbon-free surface covered with a complete monolayer of oxygen, based on the binding energies of the Ir 4f and O 1s core level peaks. During a rather long induction period with nearly constant oxygen coverage, the work function of the surface changes continuously as sensed by the gas phase O 1s signal. The sudden and rapid formation of the IrO_2 rutile phase with a thickness above 3 nm, manifested by distinct binding energy changes and substantiated by quantitative XPS analysis, provides direct evidence that the oxide film is formed via an autocatalytic growth mechanism that was previously proposed for PbO and RuO_2.

[1] Z. Novotny, B. Tobler, L. Artiglia, M. Fischer, M. Schreck, J. Raabe, J. Osterwalder*, J. Phys. Chem. Lett.*2020, 11, 9, 3601–3607.

HC-Contributed On Demand-58 A Study of Subsurface Oxygen on Ag(111) Using Density Functional Theory and Monte Carlo Simulations

Carson Mize, University of Tennessee Knoxville*; L. Crosby,* Joint Institute for Computational Sciences; University of Tennessee Knoxville*; S. Isbill,* Oak Ridge National Laboratory*; S. Roy,* University of Tennessee Knoxville

Transition metals are commonly employed as heterogeneous catalysts for the functionalization of molecules, as well as the synthesis of many bulk materials and useful commodities. One well-studied catalytic application involves the use of an oxygen rich silver surface to induce partial oxidation of ethylene to ethylene oxide. While this reaction is required as a precursor to sterilization procedures and the synthesis of ethylene glycol, the structure of the active catalyst, specifically how oxygen is adsorbed to the silver surface, has not yet been fully elucidated. Past studies suggest that atomic oxygen adsorbs to the surface as well as the region below the surface, the subsurface. To investigate the formation of subsurface oxygen at different oxygen temperatures and surface coverages, we have theoretically studied the adsorption of atomic oxygen to the surface and subsurface of Ag(111) using a combination of density functional theory (DFT), a pairwise-additive site-adsorption model, and Monte Carlo simulations. Results show that oxygen accumulates in the subsurface at surface temperatures greater than ~500 K and oxygen coverages greater than ~1/3 ML, strongly suggesting that subsurface oxygen participates in industrial oxidative catalysis. Future studies will explore the role of subsurface oxygen in surface reconstruction and catalytic mechanisms of Ag(111), as well as the formation of subsurface oxygen on Ag(110) and Ag(100) surfaces.

HC-Contributed On Demand-61 Measuring Adhesion Energies and Using them to Bridge the Gaps between Gas-Phase and Liquid-Phase Surface Chemistry, and Between Single-Crystal Metal Surfaces and Metal Nanoparticles

S. Elizabeth Harman*, G. Ruehl, J. Rumptz, C. Campbell,* University of Washington

Understanding how solvents affect the adsorption energies of catalytic reaction intermediates compared to their better-known values in gas phase is crucial for understanding liquid-phase catalysis and electrocatalysis. It has been shown that the dominant effect is a decrease in adsorption energy compared to the gas phase by an amount equal to the solvents' adhesion energies to the solid multiplied by the area per adsorbate.[1]Therefore, knowing values for solvent / solid adhesion energies is critical for understanding solvent effects in catalysis and electrocatalysis.We report here adhesion energies of liquid solvents to clean Pt(111), estimated using single crystal adsorption calorimetry (SCAC) measurements of heats of adsorption versus coverage integrated from zero coverage up to thick (bulk-like) multilayer solid films. We also present new values estimated from temperature-programmed desorption (TPD) measurements.

The adhesion energy is also the key factor that determines how strongly metal nanoparticles bind to different catalyst support materials.[2] We present SCAC measurements of the heat of adsorption of azulene to Pt(111) and show that it binds ~100 kJ/mol more strongly than naphthalene to Pt(111). Azulene has been shown to have very similar electronic character to the pentagon-heptagon (5-7)-type defects in graphene, while naphthalene resembles perfect graphene. This SCAC result therefore implies that Pt(111) binds ~100 kJ/mol more strongly to (5-7) type defects in graphene than to perfect regions of graphene.From this we estimate that the adhesion energy of Pt nanoparticles to such (5-7)-type defects in graphene will be ~0.63 J/m^2 higher (locally) than to perfect graphene surfaces.This will greatly stabilize Pt nanoparticles at such defects on graphene-like and graphite-like catalyst support materials.For example, all the Pt atoms in a 1 nm particle would be ~30 kJ/mol more stable, and have an activation energy for sintering that is ~30 kJ/mol higher, when attached to such a defect.

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HC-Contributed On Demand-64 Carbon Dissolution via Beam Reflectivity Measurements on Nickel Single Crystal Catalysts

Daniel Tinney, Tufts University*; E. High,* Rowland Institute at Harvard*; E. Dombrowski,* Commonwealth Fusion Systems*; L. Joseph, A. Utz,* Tufts University

Carbon atom diffusion on the surface and into the bulk of metal particles can modulate catalytic reactivity and film growth. Subsurface carbon diffusion is a primary step in graphene, carbon nanotube (CNT) and carbon nanofiber (CNF) growth on Ni substrates via chemical vapor deposition (CVD). Carbon build-up in the subsurface of nickel steam reforming catalysts gradually reduces catalytic activity and ultimately deactivates the metal catalyst. Traditionally, carbon diffusion is monitored using post-dose spectroscopic techniques. These methods require long wait times, temperature changes during the measurement, and correction and fitting of the spectroscopic peaks. Here, we use a novel molecular beam reflectivity approach to measure carbon diffusion and site-blocking kinetics in real time quantified on a flat Ni(111) and stepped Ni(997) surfaces. We track carbon uptake onto and into the Ni single crystal while holding surface temperature constant throughout the measurement. This new application of molecular beams allows for real-time, surface-sensitive detection of carbon dissolution into the crystal bulk at the elevated temperatures used in steam reforming (650-1000K). The onset of carbon dissolution occurs over a relatively narrow temperature range. Diffusion was found to be well fit by a Fickian model and we report bulk diffusion barriers, ED, of 137 ± 1.03 kJ mol-1 and 124 ± 0.73 kJ mol-1 for Ni(111) and Ni(997), respectively. We are also able to use the diffusion model to trace carbon and probe coverage dependent reaction trends at these elevated temperatures.

HC-Contributed On Demand-67 Trimetallic Alloys for Enhanced Ethanol Conversion to Hydrogen*, Paul Kress, Y. Wang, L. Cramer,* Tufts University*; M. Montemore,* Tulane University*; E. Sykes,* Tufts University

Understanding and controlling the structure and electronic properties of active sites is a central goal in modern catalyst research. We use a well-defined surface science and microcopy approach to characterize the structure of active sites in dilute metal alloys for a range of important reactions. Moving beyond the bimetallic paradigm, trimetallic alloys offer an additional variable with which to control active site type and properties. In this work we seek to identify a new type of catalytic site in dilute alloys - the heteronuclear dimer and small ensembles comprised of two dopant metal atoms. The reaction of interest is ethanol decomposition to acetaldehyde, hydrogen and other products with the goal of understanding the elementary steps and what sites are required for ethanol activation and conversion. Specifically, small amounts of Pt atoms in a Ag(111) host are unable to activate ethanol. Cr, which is not often investigated in model systems, also leads to limited reactivity. However, combining these two metals into an Ag host surface, as shown here at the single-atom limit, leads to cooperativity and a much higher conversion for the ethanol dehydrogenation reaction. We further understand and explain this synergy with density functional theory calculations that reveal that the mixed dimer sites have the lowest barriers for the reaction. This work demonstrates that more complex trimetallic alloys offer new and potentially useful properties with a great degree of tunability derived from their high degree of composition and structure space

HC-Contributed On Demand-70 Investigating the Alloying Mechanism of RhCu(100) and RhCu(110)*, **Yicheng Wang**,* Tufts University*; K. Papanikolaou ,* University College London, UK*; R. Hannagan,* Tufts university*; J. Schumann, M. Stamatakis,* University College London, UK*; C. Sykes,* Tufts University

Metal alloys plays a crucial role in heterogeneous catalysis and it is now fairly well established that the local coordination environment of an alloy can have a profound influence on its chemical reactivity. However, these effects can be difficult to probe in nanoparticle studies given the complexity of the active sites, nanoparticle shape and different predominantly exposed facets. On the other hand, model studies using well defined single crystal surfaces alloyed with dopants can achieve fundamental understanding of the structure-function relationship. The first step in this approach involves understanding the alloying mechanism and the type of ensembles formed. We report a combined scanning tunneling microscopy (STM) and density functional theory (DFT) study which was applied to understand the alloying behavior of Rh atoms in Cu(111), Cu(100) and Cu(110) surfaces. The STM results show a striking difference between Rh atoms alloying in Cu(111) versus the more open Cu(100) and Cu(110) surface facets.Unlike RhCu(111) where Rh atoms tend to form brim above the step edges, homogeneously dispersed Rh atoms can be observed in the terrace of Cu(100) and Cu(110). The stark different Rh distribution can be attributed to the dominance of different alloying mechanism in the Cu(111) versus Cu(100) and Cu(110) surfaces. DFT calculations show that direct atomic place exchange alloying mechanism prevails in Cu(100) and Cu(100) while Rh atoms tend to hop to a preferred sites (like step edges) before alloying in the Cu(111) surface. These model systems will serve as useful platforms for examining structure sensitive chemistry on single-atom alloys

HC-Contributed On Demand-73 2020 AVS Russell & Sigurd Varian Award Talk: Rhodium Copper Single-Atom Alloys for Selective and Coke-Free C-H Activation*, **Ryan Hannagan**[1], E. Sykes,* Tufts University

Due to the recent prevalence of small hydrocarbons, there has been renewed interest in direct dehydrogenation of small alkanes to the corresponding alkenes. One of the major issues in this reaction is the deactivation of catalysts due to coke formation. Here, we report a new RhCu single-atom alloy which displays considerable activity for C-H activation without coke formation. First, using a combination of scanning tunneling microscopy, temperature programmed desorption, and infrared spectroscopy, we characterize the model catalyst surface. We find that Rh atoms exist as isolated sites in the Cu host. We correlate this structure with the binding energy and vibrational frequency of CO on the isolated Rh sites. With knowledge of the atomic-scale structure, we then examine how the isolated Rh sites promote C-H activation. Using methyl iodide as a reporter on C-H activation, we find the isolated Rh sites promote C-H activation at a significantly lower temperature than Cu(111). We observe the formation of methane (from the hydrogenation of methyl groups) in addition to the formation of ethene (via coupling of CH_2 to CH_3 followed by beta-dehydrogenation). This is in strong contrast to extended Rh ensembles where coke formation is apparent. Together, these results indicate that RhCu single-atom alloys offer significant opportunities for efficient and coke-free C-H activation.

HC-Contributed On Demand-76 Beam Reflectivity Measurements of Ethane Dissociation on High Temperature Nickel Single-Crystal Surfaces*, **Molly Powers**, D. Tinney, L. Joseph, A. Utz,* Tufts University

Dissociative chemisorption of methane on a Ni catalyst via C-H bond cleavage is generally believed to be the rate-limiting step in the industrial steam reforming reaction. The commercial importance of this reaction, and methane's role as a model system for unravelling the energetics and dynamics of dissociative chemisorption, has resulted in extensive experimental and theoretical study including efforts to improve the absolute accuracy of DFT-based calculations of catalytically important reactions. While methane is the majority component of natural gas feedstock, ethane (C_2H_6) can also represent a significant fraction.

Previously, we used energy and vibrationally state-selected methane molecules in a supersonic molecular beam to quantify reaction probability over a wide range of energies and energetic configurations (i.e. the distribution of energy among translational, vibrational, rotational, and surface degrees of freedom). Here, we report on the extension of that approach to ethane molecules prepared with similar energy configurations. Our goal is to understand how reactivity patterns observed in the smaller methane molecule may extend to larger molecules as well as to provide accurate benchmark data for computational studies of increasingly larger and more complex molecule-surface reaction systems.

For this work, energy-resolved reaction probabilities were measured for supersonically-expanded ethane gas molecules impinging on an atomically flat Ni(111) surface. Experimental variables include a range of surface temperatures (550 K $\leq T_S \leq$ 1000 K), varying incident energies (E_i = 35 kJ/mol to > 140 kJ/mol), incidence angle, and both vibrational state-averaged and vibrational state-resolved ensembles of ethane molecules. The data provide benchmarks for computational efforts to extend chemically accurate DFT calculations to larger chemical systems, and comparisons with prior methane reactivity data on the Ni(111) surface will shed light on the role that the additional molecular complexity may play in energy flow and reactivity in larger molecules.

HC-Contributed On Demand-79 Elucidating the effect of Oxidation on the Structure and Reactivity of Rhodium Copper Single-Atom Alloys*, **Volkan Cinar**,* Tufts University*; D. Guo,* Washington State University*; A. Schilling,* Seagate Technology*; I. Waluyo,* Brookhaven National Laboratory*; J. McEwen,* Washington State University*; C. Sykes,* Tufts University

Single-atom catalysts (SACs) consisting of late-transition metals on oxide supports have recently gained significant world-wide attention due to their well-defined sites that enable more selective chemistry and the fact that they use precious metals at the ultimate limit of atom efficiency. SACs involving reducible oxide supports are good catalysts for oxidation reactions, but they tend to deactivate by sintering under reducing conditions. On the other hand, single-atom alloys (SAAs) are robust towards sintering and exhibit exceptional catalytic performance for a wide range of reactions under reducing conditions, but some SAAs deactivate under oxidizing environments. This project is aimed at systematically exploring catalytic reactivity between the SAC and SAA oxidation state extremes. Historically, bimetallic RhCu and supported Rh systems have been investigated for several reactions including CO oxidation, NO_x reduction, and the hydrogenation of hydrocarbons. Recent studies conducted on RhCu SAAs have shown that while the Rh sites bind CO strongly, CO desorbs reversibly. In contrast, model Rh/CuO_x SACs perform CO oxidation just above room temperature. However, there is a lack of understanding of structure-function relationships between these two extremes when the surface is partially oxidized. We report a study of CO oxidation on partially oxidized RhCu alloys using temperature programmed desorption (TPD), reflection absorption infrared spectroscopy (RAIRS), and low energy electron diffraction (LEED). The TPD results demonstrate that CO oxidation occurs around 456 K on an oxidized RhCu SAA. Increasing the Rh coverage led to gradual decrease of the CO oxidation temperature to 362 K at 25% of a monolayer of Rh. Isotopic TPD experiments provided evidence of a Mars van Krevelen (MvK) CO oxidation mechanism. Furthermore, more fully oxidized RhCu SAAs were inactive for CO oxidation

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[1] **AVS 2020 Russell and Sigurd Varian Awardee**

meaning that intermediate oxidation states of the SAA are most efficient for CO oxidation. LEED and IR results provide evidence for how the incorporation of Rh in the system affects its structure and the accessibility of the Rh sites to reactants. Together, these results begin to shed light on the effect of surface oxidation on the structure and reactivity of Rh sites in Cu-based SACs.

HC-Contributed On Demand-82 Investigation of CO oxidation on Rh(111) with IRRAS*, **Elizabeth Jamka**, D. Killelea,* Loyola University Chicago

Fourier-transform Infrared (FTIR) spectroscopy is a powerful technique for identification of small molecules adsorbed to metal surfaces. We have added FTIR to an 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_2on oxidized Rhodium (Rh) will be utilized as a probe reaction. We will be able to determine the chemical significance of various oxygen phases on different Rh surfaces, and the CO coverage and binding sites on the different oxygenaceous phases. 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. Past exposure conditions determined that at low temperatures, CO was observed to adsorb along (2x1)-O and RhO2 domain boundaries, and O_{sub} replenished the reacted oxygen at these boundaries at higher temperatures. When CO was prolonged exposure it consumed all O_{sub} and reacted with oxides at the defects. In recent studies, it was determined that there are multiple reaction pathways available for CO oxidation, but at temperatures at or below 350K reaction sites are not regenerate. Via FTIR, these and other reaction sites of CO oxidation will be investigated to determine reaction pathways or mechanisms.Methods developed for Rh can also be applied to other metal surfaces and small molecules of interest.

HC-Contributed On Demand-85 Study of the Effects of Co-Adsorbed Water on Acetic Acid Decomposition on Metal Surfaces*, K. Chukwu, **Hoan K.K. Nguyen**, L. Arnadottir,* Oregon State University

Acetic acid decomposition on metal surfaces and the effects of water on the decomposition are good model systems for solvent effects on small oxygenates with applications in biomass conversion. Numerous studies have found that solvents influence the selectivity and rate of heterogeneous catalytic reactions. Fundamental understanding of how water affects acetic decomposition on metal surfaces gives us valuable insight into how water changes the selectivity of decomposition reactions on different metals, further enabling bottom up design of effective catalyst and catalyst system. Here we present a combined density functional theory (DFT) calculations, microkinetic analysis and AP-XPS study of the effects of co-adsorbed water on acetic acid decomposition over Pd (111). The combination of theory and experiments is used to improve the AP-XPS analysis as well as providing atomistic insights into the mechanism. AP-XPS data show an increase in surface coverage of both chemisorbed acetic acid and acetate, while coverage of CO decreases in the presence of co-adsorbed water. MS-RGA data collected concurrently during the exposure also show an increase in the ratio of CO2(g)/CO(g) up to 80% for exposure of acetic acid with water. This supports the microkinetic analysis, where we show that in the absence of co-adsorbed water, the decarboxylation pathway (CO2) is more favorable than the decarbonylation pathway (CO) but in the presence of co-adsorbed water, the decarboxylation pathway is more favored. On Pd (111), the shift in selectivity is mostly due to changes in the OC-O bond cleavage. Water has a similar effect on the selectivity for this reaction on Pt(111) but the water has a larger effect on OC-OH bond cleavage on Pt than Pd.

HC-Contributed On Demand-88 Structure and Chemistry of Metal Surfaces at High Oxygen Coverages*, **Dan Killelea**, M. Turano,* Loyola University Chicago*; R. Farber,* The University of Chicago*; L. Juurlink,* Leiden University, Netherlands

Understanding the interaction of oxygen with transition metal surfaces is important in many areas including corrosion and catalysis. Of interest to us is the formation and chemistry of subsurface oxygen (O_{sub}); oxygen atoms dissolved in the near-surface region of catalytically active metals. The goal of these studies is to understand how incorporation of O_{sub}into the selvedge alters the surface structure and chemistry. The oxygen – Ag system, in particular, has been studied extensively both experimentally and theoretically because of its role in two important heterogeneously catalyzed industrial reactions: the epoxidation of ethylene to produce ethylene oxide and the partial oxidation of methanol to produce formaldehyde. In addition, the O/Rh and O/Ag systems serve as models for the dissociative chemisorption of diatomic molecules on close packed metal surfaces. Despite extensive research, there remain questions about the fundamental chemistry of the O/Ag system. Rh is also used in partial oxidation reactions, and its response to adsorbed oxygen provides an interesting complement to Ag. Where Ag extensively reconstructs, Rh does not. In particular, the structure of the catalytically active surface remains poorly understood under conditions of high oxygen coverages or subsurface oxygen. To improve our understanding of this system, we use ultra-high vacuum (UHV) surface science techniques to characterize Ag and Rh surfaces after exposure to atomic oxygen (AO) to obtain O coverages in excess of 1 ML. AO is generated by thermally cracking molecular O_2. We then use low-energy electron diffraction (LEED) and UHV Scanning Tunneling Microscopy (UHV-STM) to further characterize the various oxygenaceous structures produced, and quantify the amount of oxygen with temperature programmed desorption (TPD). We have found that the surface temperature during deposition is an important factor for the formation of O_{sub} and the consequent surface structures. Finally, we have recently found that Rh surfaces are significantly more reactive towards CO oxidation when O_{sub} is present. This enhanced reactivity is located at the interface between the less reactive RhO_2 oxide and O-covered metallic Rh. These results reveal the conditions under which O_{sub} is formed and stable, and show that O_{sub} also leads to enhanced reactivity of oxidized metal surfaces.

HC-Contributed On Demand-91 Surface Science at Atmospheric Pressure: Measuring Intrinsic Kinetics on Metallic Systems*, **Eric High**, E. Lee, C. Reece,* Rowland Institute at Harvard

Ultra-high vacuum surface science remains the gold standard for monitoring the elementary steps that define activity and conversion in catalysis. When combined with microkinetic modeling, these measurements have been successfully used to rationalize catalytic behavior at industrially relevant conditions. However, this method has been applied to a limited number of reactions and such pressure transferability is seen as the exception rather than the norm. We approach this problem by employing techniques with a long history of application in surface science (isotopic labeling, pulse transient measurements and model catalysis) to probe kinetic parameters at atmospheric pressure and elevated temperatures. To that end, we have built a flow system comprised of two parallel gas streams that has demonstrated a reproducible sub-second rise time upon switching. The set-up is capable of multiple experimental methodologies (steady-state flow, SSITKA, CTK, atm-TAP, atm-K&W, etc.) with no changes in configuration and the rapid rise time enables direct observation of transients inaccessible on traditional flow systems. Initial measurements have been made investigating CO oxidation on pure Pt particles to validate the instrument and to allow for a thorough and direct comparison with results from traditional surface science kinetic measurements.

HC-Contributed On Demand-94 Catalytic Enhancement Due to Coke Formation: Investigation of the Bimetallic Effect on Carbon Nanotubes Formed during Dry Reforming of Methane*, **Carly Byron**,* University of Delaware*; M. Ferrandon,* Argonne National Laboratory, USA*; G. Çelik,* Middle East Technical University, Turkey*; R. McCormick, J. Sloppy, K. Booksh,* University of Delaware*; M. Delferro,* Argonne National Laboratory, USA*; C. Ni, A. Teplyakov,* University of Delaware

Metal nanoparticles supported on metal oxides are excellent catalysts for a variety of applications, and nickel supported on MgO and Al_2O_3 has shown to be a highly active catalyst for the dry reforming of methane (DRM). Nickel is typically deposited with another transition metal to hinder surface carbon (coke) formation, often in the form of carbon nanotubes, which is assumed to deactivate the catalyst. However, recent advancements have shown that carbon nanotube formation does not always deactivate the catalyst. An in-depth analysis of the coke formation on bimetallic nickel catalysts may help us better understand the chemistry behind this phenomenon, therefore this work provides microscopic and spectroscopic characterization of the carbon nanotubes formed on various bimetallic nickel catalysts during the DRM reaction. It was determined that bimetallic promotion of nickel significantly altered the morphology of the coke formed, and that the carbon nanotubes did not affect catalytic activity due to the orientation of the nickel nanoparticle at the tips. In fact, the high catalytic activity of the nickel nanoparticles may be partially attributed to the morphology of the coke formation.

Fundamental Discoveries in Heterogeneous Catalysis Focus Topic

Room On Demand - Session HC-Invited On Demand

Fundamental Discoveries in Heterogenous Catalysis Invited On Demand Session

HC-Invited On Demand-1 Low Temperature Selective Alkane Conversion on IrO_2(110) Surfaces*, 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. Current efforts to develop a microkinetic model to explore ethylene selectivity under both TPRS and reaction conditions will be discussed.

HC-Invited On Demand-7 Alkali-promoted Copper-based Catalysts for CO_2 Activation*, W. Liao,* Stony Brook University*; **Ping Liu,*** Brookhaven National Laboratory **INVITED**

Alkalis have been reported as a promotor in the heterogeneous catalysis, being able to enhance the activity and selectivity of catalysts. The effective utilization of alkalis in catalyst optimization requires the fundamental understanding of underlying mechanism. This presentation will take potassium (K)-modified Cu_xO/Cu(111) (x≤2) model surface as a case study to rationalize the nature of K during the carbon dioxide hydrogenation using combined density functional theory (DFT) calculation and the kinetic Monte-Carlo (KMC) simulation. The result demonstrates the significant tuning of selectivity from carbon monoxide to methanol on going from Cu(111) to K-modified Cu_xO/Cu(111). The deposited K^+ stabilizes the Cu_xO thin film under the reducing condition of carbon dioxide hydrogenation. More importantly, our study reveals that K^+ acts as an active center for selective tuning in the binding, an accelerator for charge transfer, and a mediator for the electron tunneling. As a result, the K-modified Cu_xO/Cu(111) opens a methanediol [$H_2C(OH)_2$]-mediated Formate pathway to facilitate the selective conversion of carbon dioxide to methanol. Our study develops the intrinsic rules of design to tune the catalytic performance using alkali metals.

HC-Invited On Demand-13 Influence of Water on C-O Hydrogenolysis Catalyzed by Ru/TiO_2*, D. Stuck, A. Mahdavi-Shakib,* University of Maine*; R. Austin,* Barnard College*; L. Grabow,* University of Houston*; B. Frederick, **Thomas J. Schwartz,*** University of Maine **INVITED**

Several groups have recently shown the importance of metal-TiO_2 interfacial sties for selective activation of oxygen in a variety of reactions, including hydrodeoxygenation of phenolics.Our team has previously shown that TiO_2-supported catalysts containing small Ru nanoparticles are highly active for the conversion of phenol to benzene, which is consistent with the results from Crossley and coworkers, who have shown the reaction to occur at the Ru-TiO_2 interface.Both observations can be explained by a mechanism wherein surface hydroxyls present on the TiO_2 surface in the immediate vicinity of the Ru nanoparticles are protonated during heterolytic H_2 dissociation, leading to acidic Ti-$OH_{2\text{-}}$ surface species.Phenol then adsorbs across the Ru-TiO_2 interface, and the acidic proton from Ti-OH_2 facilitates C-O scission, regenerating the Ti-OH moiety and leaving a phenyl ring to be hydrogenated on the Ru surface.This mechanism is predicted to be favorable in the presence of water, and reports from the literature indicate an enhancement in the amount of benzene produced ranging from 30% to 200%, depending on the fugacity of water in the system. In this work, we seek to clarify the role of water in C-O hydrogenolysis catalyzed by Ru/TiO_2- materials.

We measured reaction orders for phenol hydrogenolysis over Ru nanoparticles supported on two different TiO_2 materials: pure anatase TiO_2 and pure rutile TiO_2.The phase of water and phenol is verified based on thermodynamic calculations, which show that 85% of the material exists as a vapor.The 15% which exists as a liquid is hypothesized to be trapped in the pore structure of the catalyst, indicating that the reaction should occur in the liquid phase.The reaction is positive-order with respect to water for Ru/rutile and negative-order for Ru/anatase, which correlates with differential heats of irreversible water adsorption on TiO_2 powders that show stronger binding of water to anatase TiO_2 than to rutile $TiO_{2\text{-}}$. The kinetics are consistent with a rate expression in which water inhibits the reaction by strong binding to Ru-TiO_2 interface sites. Kinetic Monte Carlo results for a catalyst consisting of a Ru nanorod supported on a rutile TiO_2 surface suggest that water-related species are abundant at the Ru-TiO_2 interface at high water pressures, and that as the temperature is lowered these abundant species can lead to the inhibitory effect observed in our kinetics data.The observed reactivity trends are correlated with the surface hydroxyl features of the TiO_2 support, as we have recently observed using FTIR spectroscopy.

HC-Invited On Demand-19 Reversible Surface Transformation Enables the Revivification of Mixed Metal Hydroxide Water Oxidation Catalysts*, C. Kuai, **Feng Lin,*** Virginia Tech **INVITED**

The electrode-electrolyte interfacial reactivity and stability govern the efficiency and lifetime of electrochemical devices, especially under aggressive reaction conditions such as high temperature, high potential, and corrosive environments. Modulating the metal-oxygen bonding environment at the electrode surface offers an effective path towards enhancing the interfacial reactivity. However, the high interfacial reactivity can trigger undesired interfacial reactions that lead to local structural changes, phase segregation and dissolution, and ultimately the complete degradation of the pre-designed metal-oxygen bonding environment. The rational design of a highly active and stable electrocatalyst is largely hindered by this dilemma. Understanding how the electrocatalyst-electrolyte interface transforms under operating conditions can generate mechanistic insights into identifying the catalytically active motif and establishing methodologies to circumvent the dilemma by repairing the degraded structure. In this presentation, we report that *operando* synchrotron spectroscopic and microscopic analyses suggest that the interfacial degradation can be reversible between catalytic oxidation and reduction potentials. Such reversibility allows us to develop an intermittent reduction methodology to revivify the catalytic activity under operating conditions, enhancing catalyst durability.

HC-Invited On Demand-25 Designed Metal Release from Complex Metal Oxides*, **Sara Mason,*** University of Iowa **INVITED**

Nanoscale complex metal oxides have transformed how technology is used worldwide. The most widespread examples are the electroactive components of Li-ion batteries found in portable electronic devices. As the number of portable devices is projected to increase, so too will the inadvertent release of complex metal oxide nanomaterials into the environment. This is a pressing problem because the environmental and biological impact of complex metal oxide nanomaterials are most times unknown, since they are subject to transform rapidly with changes in pH and concentration. This brings us to a looming problem that needs to be solved on a global scale. There is a fundamental knowledge gap in developing sustainable nanotechnology because there is not yet a systematic method to predict how the properties of a complex metal oxide will change with changes in chemical environment. We have adapted and developed a method that combines DFT-computed total energies and experimentally adjustable reaction conditions to compute the cation release of complex metal oxides. We focus on the materials found in a Li-ion battery cathode, namely LiCoO2 (LCO) and compositionally tuned variants with general chemical formula Li(NixMnyCoz)O2 (NMC). We find that adjusting surface terminations, compositions and pH will change the dissolution properties of this family of materials, and ultimately lead to increased favorability of metal release. We go on to propose a new set of materials, with maintained function, based on non-toxic and abundant metals, thereby reducing the biological impact. We then predict the thermodynamics of metal release to give insight on tailorable properties that can be used to formulate sustainable design principles for future generations of functional complex metal oxide materials.

HC-Invited On Demand-31 Hydrogenation of CO_2 to Methanol on Metal-Oxide and Metal-Carbide Interfaces*, **Jose Rodriguez**,* Brookhaven National Laboratory **INVITED**

The high thermochemical stability of CO_2 makes very difficult the catalytic conversion of the molecule into alcohols or other hydrocarbon compounds which can be used as fuels or the starting point for the generation of fine chemicals. Pure metals and bimetallic systems used for the $CO_2 \rightarrow CH_3OH$ conversion usually bind CO_2 too weakly and, thus, show low catalytic activity. Here, I will discuss a series of recent studies that illustrate the advantages of metal-oxide and metal-carbide interfaces when aiming at the conversion of CO_2 into methanol. CeO_x/Cu(111), Cu/CeO_x/TiO_2(110) and Au/CeO_x/TiO_2(110) 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 Au-ceria interfaces, the multifunctional combination of metal and oxide centers leads to complementary chemical properties that open active reaction pathways for methanol synthesis. Efficient catalysts are also generated after depositing Cu and Au on TiC(001). In these cases, strong-metal support interactions modify the electronic properties of the admetals and make them active for the binding of CO_2 and its subsequent transformation into CH_3OH at the metal-carbide interfaces.

HC-Invited On Demand-37 Chirality Detection of Surface Desorption Products using Photoelectron Circular Dichroism*, J. Wega, **Tim Schäfer**, G. Westphal,* University Göttingen, Germany **INVITED**

Chirality detection of gas-phase molecules at low concentrations is challenging as the molecular number density is usually too low to perform conventional circular dichroism absorption experiments. In recent years, new spectroscopic methods have been developed to detect chirality in the gas phase. In particular, the angular distribution of photoelectrons after multiphoton laser ionization of chiral molecules using circularly polarized light is highly sensitive to the enantiomeric form of the ionized molecule (multiphoton photoelectron circular dichro-ism (MP-PECD)). In the talk, I will present the MP-PECD as an analytic tool for chirality detection of the bicyclic monoterpene fenchone desorbing from a Ag(111) crystal. We recorded velocity resolved kinetics of fenchone desorption on Ag(111) using pulsed molecular beams with ion imaging techniques. In addition, we measured temperature-programmed desorption spectra of the same system. Both experiments indicate weak physisorption of fenchone on Ag(111). We combined both experimental techniques with enantiomer-specific detection by recording MP-PECD of desorbing molecules using photoelectron imaging spectroscopy. We can clearly assign the enantiomeric form of the desorption product fenchone in sub-monolayer concentration. The experiment demonstrates the combination of MP-PECD with surface science experiments, paving the way for enantiomer-specific detection of surface reaction products on heterogeneous catalysts for asymmetric synthesis.

Advanced Ion Microscopy and Ion Beam Nano-engineering Focus Topic

Room On Demand - Session HI-Contributed On Demand

Advanced Ion Microscopy & Nano-Engineering Contributed On Demand Session

HI-Contributed On Demand-1 Applications of the Cesium Low Temperature Ion Source*, **Adam Steele**, A. Schwarzkopf,* zeroK NanoTech Corporation*; B. Knuffman,* zeroK NanoTech Corporation

We present the latest results from FIB and FIB+SIMS systems featuring the Cs⁺ Low Temperature Ion Source (LoTIS). When compared with other ion sources LoTIS can deliver very small spot sizes, high sputter rates, high yields of secondary ions, and a wide range of beam currents from pA to many nA.

We will review applications of LoTIS tested on a single beam FIB system. These include high resolution imaging, long depth-of-focus imaging, successful circuit edit operations on 10 nm node integrated circuits, high-precision machining of gold, and demonstration of the high grain-visibility imaging in copper and steel offered by LoTIS.

Previously we reported spot sizes as small as (2.1 ± 0.2) nm (one standard deviation) are observed with a 10 keV, 1.0 pA beam. Brightness values as high as (2.4 ± 0.1) × 107 A m-2 sr-1 eV-1 are observed near 8 pA [1]. The measured peak brightness is over 24 times higher than the highest brightness observed in a Ga liquid metal ion source (LMIS). This system has generated beam exceeding 11 nA. LoTIS is composed of a several discrete stages that collect, compress, cool and finally photoionize a cesium atomic beam [2].

The talk will conclude by reviewing our progress in the construction of a high resolution FIB/SIMS hybrid system called SIMS:ZERO; this system is being built in collaboration with the Luxembourg Institute of Science and Technology (LIST). SIMS:ZERO will be capable of high-resolution FIB operations while also providing a new material analysis information channel through the application of Secondary Ion Mass Spectrometry (SIMS). For many target materials Cs+ will generate orders or magnitude more secondary ions than other ion ions. In addition, LoTIS is can provide over 100x more current into a given spot than alternative Cs⁺ ion sources.

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HI-Contributed On Demand-7 Focused Nanoscale Machining via the Gas Field Ion Microscope with Laser and Reactive Ion Assist: Joint Experimental and Simulation Investigations*, **Jack Lasseter**, P. Rack,* University of Tennessee Knoxville

Focused ion beams utilizing light atoms like helium and neon are able to be used in materials processing providing nanoscale manipulation from milling, to reactive ion etching, to 3D nanomaterials deposition. However very light atoms like helium require high doses for milling applications and thus can suffer sub-surface implantation effects like substrate damage through bubbling, so nanofabrication can require extra care. Thus, reactive ion and laser-assisted focused ion beam techniques can be used to enhance the sputtering and thus minimize sub-surface damage. To emulate focused ion beam nanomachining, we have developed the EnvizION simulation code, which at its core uses SRIM/TRIM statistical descriptions of ion-solid interactions to model 3D substrates through a voxelized substrate.

The nanoscale resolution and ability to image insulating samples provides ion microscopes formidable nanofabrication abilities. In this presentation we will overview our groups recent experimental work in gas field ion nanomachining and complement the experiments with various EnvizION simulations. Applications include defect generation in two-dimensional materials such as transition metal dichalcogenides, gas assisted deposition to print 3D PtC structures from a $(CH_3)_3Pt(C_pCH_3)$ gas precursor, and laser + XeF_2 gas pulsing methods to enhance the material removal rate of WSe_2 and SiO_2. The laser assisted XeF_2 has been shown to enhance the etch yield by 9x relative to a pure helium sputtering process. Finally, we have incorporated reactive gas etching in the EnvizION simulation and have performed an exhaustive comparison with both Ga⁺ and Ne⁺ milling and XeF_2 reactive etching. Since the subsurface damage is a function of the dose these types of enhancements are stepping stones to overcome damage related roadblocks.

*The authors Acknowledge Shida Tan, Rick Livengood, AmirYuval Greenzweig, and Amir Raveh of Intel for their support and contributions to the development of the EnvizION simulation.

HI-Contributed On Demand-10 Imaging of SARS-CoV-2 infected Vero E6 Cells by Helium Ion Microscopy*, **Natalie Frese**,* Bielefeld University, Germany*; P. Schmerer,* Justus-Liebig-University Giessen, Germany*; M. Wortmann,* Bielefeld University of Applied Sciences, Germany*; M. Schürmann ,* Bielefeld University, Germany*; M. König,* Justus-Liebig-University Giessen, Germany*; M. Westphal,* Bielefeld University, Germany*; F. Weber,* Justus-Liebig-University Giessen, Germany*; H. Sudhoff, A. Gölzhäuser,* Bielefeld University, Germany

Helium ion microscopy (HIM) enables the visualization of biological samples such as cellular structures, virus particles, and microbial interactions with sub-nanometer resolution, large depth of field, and high surface sensitivity. The charge compensation capability of the HIM allows imaging of insulating biological samples without conductive coatings. In this contribution, the first HIM images of uncoated SARS-CoV-2 infected Vero E6 cells are presented [1]. Several areas of interactions between cells and virus particles, as well as among virus particles, were imaged. The images show the three-dimensional appearance of SARS-CoV-2 on the surface of Vero E6 cells and demonstrate the potential of the HIM in bioimaging, especially for the imaging of interactions between viruses and their host organisms.

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Advanced Ion Microscopy and Ion Beam Nano-engineering Focus Topic
Room On Demand - Session HI-Invited On Demand
Advanced Ion Microscopy & Nano-Engineering Invited On Demand Session

HI-Invited On Demand-1 Nanoscale Vortex Pinning Structures in High-Temperature Superconductors Created in a Helium Ion Microscope*, Wolfgang Lang*, *B. Aichner,* University of Vienna, Austria*; M. Karrer, K. Wurster,* Universität Tübingen, Germany*; V. Misko,* Universiteit Antwerpen, Belgium*; K. Mletschnig,* University of Vienna, Austria*; M. Dosmailov,* Al-Farabi Kazakh National University, Kazakhstan*; J. Pedarnig,* University of Linz, Austria*; F. Nori,* RIKEN, Japan*; R. Kleiner, E. Goldobin, D. Koelle,* Universität Tübingen, Germany **INVITED**

The focused beam of a helium ion microscope is used to fabricate ultradense patterns of superconducting/insulating domains in thin films of the prototypical cuprate superconductor $YBa_2Cu_3O_{7-\delta}$ (YBCO) with unprecedented lateral resolution down to 40 nm. Simulations of the He^+ ion-target interactions [1] reveal 3-dimensional defect landscapes and allow one to determine the distribution of local critical temperatures in the material. The simulations anticipate that well-defined patterns of non-superconducting material in the superconducting matrix can be created with low blurring by focused 30 keV He^+ ion irradiation.

In such engineered defect patterns, the behavior of magnetic flux quanta, called Abrikosov vortices or fluxons, is investigated in view of emerging superconducting electronics, known as fluxonics. As an initial step along this route vortex commensurability effects are investigated that result from trapping fluxons at the engineered defects [2]. We report on the observation of novel commensurability effects in ultradense kagomé-like pinning patterns, where a competition between vortex pinning and the elastic energy of the distorted vortex lattice leads to unusual matching effects, as revealed by transport measurements and molecular-dynamic simulations [3]. Other intriguing observations in these ultradense superconducting patterns like vortex ratchet effects will be also discussed.

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HI-Invited On Demand-7 Cluster Ion Beams: A New Tool for Characterization and Processing of Organic and Biological Materials*, Jiro Matsuo,* Quantum Science and Engineering Center, Kyoto University, Japan **INVITED**

Ion beams have been utilized for various applications, such as implantation, sputtering, etching and thin film formation for inorganic materials. However, it is quite difficult to apply ion beam technique for organic materials, because organic materials are easily decomposed with ion bombardments. This is due to the fact that bonding energy in organic molecule is much lower than a kinetic energy of ions. Recently, organic materials, such as functional-polymer, organic semiconductors and biological materials, are of interest in not only fundamental research but also many industrial applications. It has been demonstrated that large cluster ion beams have a great potential to sputter organic molecules without any residual damage on the surface, because cluster ion beams are equivalently low energy ion beams. Energy of cluster ion is shared with the constituent atoms in the cluster ion. For instance, when large Ar cluster ions with the cluster size of 1000 are accelerated with 10keV, each constituent atom has only 10eV/atom, which is comparable for binding energy of organic molecules. Therefore, cluster ion beams are now widely utilized for organic depth profile measurements in XPS or SIMS. More than 70% of those surface analysis system is delivered with GCIB source. It has been confirmed that no or very little damage is introduced on organic surfaces after large cluster ion bombardments. However, there is no report on molecular structure of sputtered species from organic materials. Sputtered molecules from PMMA were captured on Si wafers and measured with XPS technique. C 1s core level spectrum was almost identical to that of pristine PMMA. This measurement reveals that most of the carbon atoms have very similar chemical structures, but it is very difficult to measure molecular structures. We have also developed a finely focused large cluster ion beam (~1mm) for the primary ion beam for use in SIMS [1] and combined it with mass spectrometers of the quadrupole time-of-flight mass spectrometry (Q-TOF) type without pulsing primary ions. This mass spectrometer is equipped with MS/MS capability and allows to determine the structure of the secondary ion by using the collision-induced dissociation (CID) technique. This new system allows us to characterize 3D distribution of organic molecules.Fundamental phenomena of cluster ion collision with organic molecules will be discussed in conjunction with possible applications.

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Leaders in Energy and the Environment Focus Topic
Room On Demand - Session LD-Contributed On Demand
Leaders in Energy and the Environment Contributed On Demand Session

LD-Contributed On Demand-1 Work Function Reduction of Carbon Nanospikes and the Effects of Contaminants by XPS and UPS*, Arthur Baddorf*, *D. Hensley,* Oak Ridge National Laboratory*; A. Rondinone,* Los Alamos National Laboratory

Carbon nanospikes show excellent energy and selectivity for electrochemical conversion of CO_2 to ethanol and N_2 to NH_3. Transmission electron microscopy (TEM) images reveal that these nanospikes are 50- 80 nm in height and terminated with a sharp tip of radius ~1 nm. It has been proposed that catalytic activity follows from an enhanced electric field from the sharp spike topography. We have tested this hypothesis through measurements of the absolute work function 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 produces 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.

Contamination of the spiked surface raises the work function above that of the clean nanospikes. Work function values after exposure are 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 from as-grown nanospike samples and is reproduced by 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 research was conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility

LD-Contributed On Demand-4 Electrochemical Performance of $CaFe_2O_4$ Synthesized at Multiple Fuel-to-Oxidizer Ratios*, Jacob Strimaitis*, *S. Danquah, C. Denize, C. Bonner, S. Pradhan, M. Bahoura,* Norfolk State University

Porous $CaFe_2O_4$ (pCFO), a promising conversion-type anode material for next-generation lithium-ion batteries (LIB) and hybrid supercapacitors (HSC), is relatively easy to produce via solution combustion synthesis (SCS). However, despite evidence that the morphology, composition, and electrochemical performance of metal oxides can be enhanced by changing the fuel-to-oxidizer ratio during SCS, such treatment has yet been applied to pCFO. In this study it is demonstrated that increasing the ratio across a “moderately fuel-lean” to “moderately fuel-rich” range increases the porosity, inter-particle conglomeration, and specific capacity of pCFO, further cementing the importance of stoichiometric considerations in SCS. Future implications of extending the range of the ratio and optimizing calcination temperature and time in order to reach the theoretical capacity target are also discussed.

LD-Contributed On Demand-7 Modern Devices from Old Materials - Selenium and Selenium-Tellurium Alloys Thin Film Solar Cells*, Ido Hadar,* The Hebrew University of Jerusalem, Israel*; T. Song, W. Ke, X. Hu, Z. Luo, V. P. Dravid, M. Kanatzidis,* Northwestern University

The photovoltaic properties of selenium were discovered about 150 years, and shortly afterward, selenium was utilized to fabricate the first 'thin-film' solar cell. This discovery led to modern research of semiconductors and development of related technologies. Selenium was implemented in many of these devices and applications. Following the rise of alternative semiconductors, and specifically silicon, the usage of selenium slowly declined. In recent years, the search for simple and scalable photovoltaic materials has revived the research of selenium as an elemental semiconductor that may be implemented as a possible absorber for extremely low-cost and highly scalable solar cells. Selenium has few desirable properties for these devices such as high absorption coefficient, intrinsic environmental stability, and low-temperature fabrication (below 200°C).

Herein we study the main parameters that define the quality and efficiency of selenium-based thin-film solar cells, fabricated by vacuum thermal evaporation, and optimize them using modern tools and approach. We found that careful annealing of the selenium film, very close to its melting temperature, is essential to obtain high-quality crystalline films. Moreover, the anisotropic structure of selenium, composed of 1D chains, suggests that alignment of the crystals in the thin film may improve the device properties, and we study the means to control the film orientation. Finally, we indicate the importance of light illumination (and excitation) of the film during the annealing process, enhancing and improving the film's crystallization.

Following these results, we study how the selenium bandgap (1.7 eV), can be tuned to the optimal value for photovoltaic absorber (1.2-1.4 eV), by alloying selenium with the isomorphic low bandgap semiconductor tellurium. Selenium-tellurium alloys exhibit a strong non-linear shift of the conduction band minimum energy, leading to a non-linear decrease of the bandgap. Consequently, the desired bandgap energy can be obtained by alloying a relatively small amount of tellurium (~10%). Thin-film solar cells based on the selenium-tellurium alloy indeed show improved current density and spectral response due to the optimized bandgap. The overall efficiency of the selenium-tellurium devices is still lower than the pure selenium devices, due to lower voltage and fill-factor. We indicate the leading causes for the lower properties and suggest how to resolve them and improve the device efficiency.

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LD-Contributed On Demand-10 A Combined DRIFTS and Theoretical Study of the Mechanisms of Aldol Condensation of Acetaldehyde on CeO_2(111)*, Suman Bhasker-Ranganath, M. Rahman, C. Zhao,* Louisiana State University*; F. Calaza,* Instituto de Desarrollo Tecnoloǵico para la Industria Química , Argentina*; Z. Wu,* Oak Ridge National Laboratory*; Y. Xu,* Louisiana State University

Aldol condensation creates C-C bonds between organic oxygenates, providing a useful pathway for upgrading of biomass-derived feedstock to fuels and higher value chemicals. To develop a better understanding of this reaction and factors that limit activity and selectivity on ceria, we have explored the reaction pathways for self-condensation of acetaldehyde (AcH) to crotonaldehyde (CrH) on ceria nano-octahedra using diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), and modeling based on DFT calculations.

As opposed to a lack of C-C coupling activity in UHV,[1] we find that CrH forms readily on ceria nano-octahedra at ambient temperature under a flow of AcH. All major peaks detected in DRIFTS are assigned conclusively by comparison with simulated IR spectra to either AcH*, *trans*-CrH*, or a stable intermediate state, as adsorbed on CeO_2(111). The reaction on stoichiometric sites proceeds through enolization of AcH and C-C coupling between the enolate and molecular AcH. The C-C coupled intermediate transforms into 3-hydroxylbutanal (3HBtL), which further enolizes and dehydroxylates to form CrH. A slightly less stable *cis* isomer of CrH* forms via the same reaction pathway with different molecular orientations in C-C coupling, but the *trans* isomer is more stable and is estimated to dominate in coverage. The reaction, when occurring on a point surface oxygen vacancy (V_O), leads to a build-up of the enolate of 3HBtL/V_O, with a 1620 cm^{-1} peak in the DRIFTS spectra that is assigned to νC=C mode of this intermediate. Desorption of CrH from V_O is much more hindered than from stoichiometric sites, so V_O is not an active site at ambient temperature.[2]

Analysis of the reaction kinetics suggests that, the desorption-limited reaction rate should be zero-order in AcH partial pressure if the surface is mostly occupied, or second-order if the reaction is at low conversion. For this and similar reactions, therefore, enhancing facile product desorption would be key to having a workable catalyst based on ceria or similar oxides.

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LD-Contributed On Demand-13 Atomic-Scale Insights Into the Workings of Pt-Based Copper Oxide Single-Atom Catalysts*, Audrey Dannar, A. Schilling, G. Giannakakis, A. Therrien, C. Sykes,* Tufts University

Single-atom catalysts are often comprised of isolated metal atoms anchored on oxide supports and have recently gained considerable attention for their improvements in selectivity and reactivity for important industrial reactions such as preferential oxidation of CO. We have previously shown that single Pt atoms on an atomically thin copper oxide film grown on Cu(111) 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 experiments 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 preferentially activate CO but not H_2. These results were then used to design a nanoparticle catalyst analog which functions under industrially relevant preferential oxidation of CO in H_2 (CO-PROX) conditions. Moving beyond this initial work which made use of a thin film oxide, we are now in the process of characterizing the 111 facet of a bulk Cu_2O single-crystal. This will provide a useful model catalyst surface as it better mimics the Cu_2O particles present in high surface area catalysts. Taken together, our thin-film and bulk copper oxide surfaces with isolated Pt atoms further the atomic-scale understanding of single-atom catalysts which should aid in the rational design of next-generation catalysts.

Leaders in Energy and the Environment Focus Topic
Room On Demand - Session LD-Invited On Demand

Leaders in Energy and the Environment Invited On Demand Session

LD-Invited On Demand-1 Atomic-Scale Imaging of Optically-Active Nanoscale Systems*, Jeffrey R. Guest,* Argonne National Laboratory **INVITED**

Optical interactions and photophysical processes hinge on structure and the local environment in nanoscale systems, it is critically important to develop experimental approaches which can characterize these optical properties and correlate them with atomic-scale morphology and electronic structure. Over the past three decades, ultra-high vacuum (UHV) scanning tunneling microscopy/spectroscopy (STM/STS) and associated surface preparation techniques have demonstrated atomic-scale control over nanoscale structures.In parallel, single-particle laser spectroscopy has elucidated photophysics, quantum coherence, and optical properties with ultrahigh spectral resolution at the single quantum absorber and emitter level.

In this talk, I will focus on our efforts to extend these studies to the atomic scale on surfaces by combining UHV STM and single particle laser spectroscopy. I will discuss our work exploring the structural, electronic, and transport properties of donor-acceptor molecular heterojunctions (HJs) self-assembled from C60 and pentacene as a potential platform for exploring photophysics at the molecular scale. We have resolved a surprising structure and charge transfer in in-plane molecular HJs [1], and demonstrated extremely strong (and spatially dependent) current rectification in transport for a stacked molecular HJ at the monolayer level [2].I will discuss recent STM/STS measurements on defects in bilayer WSe_2, which may be related to the single-photon emitting defects observed in laser spectroscopy experiments, revealing the local electronic structure and demonstrate the ability to control the charge state of these defects [3]. Time permitting, I will discuss UHV STM measurements on Cu2O (111) and

(110) surfaces and our efforts to understand their physical and electronic structure in light of their photocatalytic activity [4].

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LD-Invited On Demand-7 Probing Molecule-Substrate Interactions at Angstrom Scale by Ultrahigh Vacuum Tip-Enhanced Raman Spectroscopy*, Nan Jiang,* University of Illinois at Chicago **INVITED**

To demonstrate the effect of local environments on complex chemical systems, we designed a series of tip-enhanced Raman spectroscopy (TERS) experiments to study molecule-substrate interactions at angstrom scale. We chose subphthalocyanine molecules deposited on a Ag(100) surface as an example of weak interactions between the molecules and the substrate. We were able to ascertain subtle vibrational modes which showed an excellent agreement between experimental spectra and simulated Raman spectra of gas phase molecules. In another case, a strong interaction with the surroundings leads to symmetry breaking, allowing us to separately detect intermolecular interactions such as electrostatic attractions by using TERS. In combination with theory, we revealed the lifting of vibrational degeneracy inside a molecular self-assembly due to strong lateral intermolecular interactions. To address the inability of scanning tunneling microscopy (STM) to study the configurations of adsorbed non-planar molecules on surfaces, we used TERS to unambiguously determine the tilt or orientation of molecules on a surface. Due to the selection rules for TERS, vibrational modes that are perpendicular to the surface and parallel to the tip and enhanced EM field are the most strongly enhanced. Since TERS spectra rely upon molecular orientation, we identified multiple orientations of rubrene on a Ag(100) surface. The sensitivity of TERS to molecular orientation combined with our 5.5 angstrom spatial resolution demonstrates a unique analytical technique for similar non-planar molecules. We also reported the first demonstration of STM-TERS towards the study of isomeric nonplanar adsorbates on three different well-defined substrates, Ag(100), Cu(100) and Au(100). We demonstrated the effects of surface interactions on the vibrational modes of molecules, indicating that the substrate is an intriguing parameter to manipulate the self-assembly and configurations of ad-molecules. Together, our work allows the definitive identification of multiple orientations of individual molecules and their dependence upon highly localized chemical environments.

LD-Invited On Demand-13 HAXPES for Device Applications: From the Surface into the Bulk*, Anna Regoutz,* University College London, UK **INVITED**

X-ray photoelectron spectroscopy (XPS) is based on the photoelectric effect discovered and described by Planck, Einstein and Millikan, and has its beginnings in the ground breaking work of Kai Siegbahn, who received the Nobel Prize in Physics in 1981 for the development of the technique. XPS can non-destructively probe the chemical composition, local chemical environments, and electronic structure of matter, and since its invention it has been applied to a vast range of materials, including solids, liquids, and gases. The most common variety of XPS uses soft X-ray sources, e.g. Al Kα at 1.5 keV, giving extremely surface sensitive results probing only the first few nanometres of a sample's surface.

Hard X-ray excitation sources with energies of up to 10 keV extend the probing capabilities of XPS beyond the outermost surface of materials by enabling photoelectrons from much deeper regions to be detected. Hard X-ray photoelectron spectroscopy (HAXPES) delivers much greater probing depths of tens of nanometres enabling the characterisation of buried layers and interfaces in structured materials, e.g. thin film stacks and core-shell nanoparticles, as well as bulk characteristics of homogeneous samples. Like XPS, HAXPES enables the study of both chemical states and electronic structure. Over the last decade the development of advanced beamlines at synchrotrons in parallel with the advent of laboratory-based spectrometers has opened up HAXPES for a much wider range of materials and applications.

This talk will give an introduction to the general capabilities of HAXPES. It will provide an overview of the additional challenges and opportunities that HAXPES presents and will cover recent developments and results of this emerging technique.

LD-Invited On Demand-19 Nanoparticle Size, Shape, Composition and Support Effects in the Hydrogenation of Carbon Dioxide*, Beatriz Roldan Cuenya,* Fritz-Haber Institute of the Max Planck Society, Germany **INVITED**

The selective hydrogenation of CO_2 to methanol and high-order hydrocarbons is a promising process for establishing a methanol economy and recycling CO_2. Although for the methanol synthesis there is a well-established industrial process based on a $Cu/ZnO/Al_2O_3$ catalyst, open questions still remain relative to the reaction mechanism and the active phases involved. The same applies to the "modified" Fischer-Tropsch process commonly catalyzed by Fe-based materials where the oxidation state of the active catalyst and the possible formation of carbide species is debated.

Since these reactions are catalyzed by nanostructured materials, tailoring their chemical reactivity at the atomic level will be the challenge to address. In order to accomplish this, we must first obtain a fundamental understanding of the structural and chemical properties of complex nanoscale systems. In addition, the dynamic nature of the nanoparticle (NP) catalysts and their response to the environment must be taken into consideration. To address the complexity of real-world nanocatalysts, a synergistic approach taking advantage of a variety of cutting-edge experimental methods (AFM, TEM, TPD, NAP-XPS, XAFS, MS/GC) has been undertaken.

Catalytically active size- and shape-controlled NPs (Fe, Cu, Cu-Zn, Cu-Ni, Cu-Ga) will be synthesized via colloidal chemistry and compared to model NP systems synthesized via physical vapor deposition. Structure/composition-reactivity correlations *in situ* and under realistic *operando* reaction conditions, i.e., at high pressure will be investigated. In particular, the role of the NP size, shape (spherical vs cubic NPs), surface composition (alloy, core-shell) and support (ZnO, Al_2O_3, ZnOAl, SiO_2, ZrO_2) in the activity and selectivity will be addressed. Our results are expected to provide the required fundamental understanding that might lead to new routes for the reutilization of CO_2 through its direct and selective conversion into valuable chemicals such as methanol or high order hydrocarbons.

New Trends in Structural Electronic Characterization of Materials, Interfaces, and Surfaces Using Synchrotron and FEL Based Light Sources Focus Topic

Room On Demand - Session LS-Contributed On Demand

New Trends in Structural Electronic Characterization of Materials, Interfaces, and Surfaces Using Synchrotron and FEL Based Radiation Sources Contributed On Demand Session

LS-Contributed On Demand-1 Resolving Interfacial Electronic Structure in Thin Film Heterostructures using Resonant X-ray Reflectometry*, Ryan Need,* University of Florida

The interfaces between electronic materials are critically important for the operation of modern electronic devices and the pursuit of new knowledge in solid state physics. Today, the interest in electronic interfaces is fueled by emerging technologies like quantum computing, spintronics, and energy storage, along with fundamental questions about how tuning symmetry and band topology at interfaces can modify functional properties. Answering these questions requires the development of characterization probes that have high spatial and spectral resolution, a wide range of sample environments, and are compatible with in-situ or in-operando experiments.

In this talk, we argue that resonant X-ray reflectometry (RXR), which combines the element-specificity and local structure sensitivity of X-ray absorption spectroscopy with the Angstrom depth-resolution of reflectometry, is the probe best suited to this challenge. As an example, we show how RXR can be used to extract electronic structure depth profiles in complex oxide superlattices and visualize interfacial charge transfer with atomic layer resolution. Specifically, we present measurements collected from $SmTiO_3$(SmTO)/$SrTiO_3$ (STO) superlattices with STO quantum wells varying in thickness from five SrO planes to a single SrO plane. At the polar-nonpolar SmTO/STO interface, a known electrostatic discontinuity leads to approximately half an electron per areal unit cell transferred from the interfacial SmO layer into the neighboring STO quantum well. We observe this charge transfer as a suppression of the Ti t_{2g} absorption peaks that minimizes contrast with the neighboring SmTO layers at those energies and leads to a pronounced absence of superlattice peaks in the reflectivity data. Critically, our results demonstrate the sensitivity of RXR to electronic reconstruction in the monolayer limit and prove RXR to be a powerful means of characterizing interfacial electronic structure in quantum materials.

LS-Contributed On Demand-4 HAXPES Study of Surface/Interface Effects Induced by Heavy Alkali Post Deposition Treatment of (Ag,Cu)(In,Ga)se2 Thin Film Solar Cell Absorbers*, **Natalia Martin,*** Uppsala University, Sweden*; T. Törndahl,* Uppsala University , Sweden*; K. Simonov,* Department of Materials and Process Development Swerim AB, Sweden*; H. Rensmo, C. Platzer-Björkman,* Uppsala University, Sweden

Solar cells based on Cu(In,Ga)Se_2 (CIGS) thin film absorbers have shown high and stable efficiencies for both laboratory cells and industrial modules with recent record cell efficiencies of 23.4% [1]. In order to reach closer to the theoretical maximum efficiency of around 30%, further reductions of optical and electrical losses are needed. Some recent works show that silver (Ag) alloying in CIGS to form (Ag,Cu)(In,Ga)Se_2 (ACIGS) leads to higher device efficiencies as compared to similar CIGS devices without Ag [2]. More, a postdeposition treatment (PDT) based on the alkali metal fluorides (i.e., KF, RbF or CsF) [3] after absorber formation has been studied recently and is known to improve the efficiency in CIGS solar cells, mainly by an increase in the open circuit voltage, V_{OC}. The exact role of the silver and/or alkali elements is intensively discussed, but it is clear that interface and grain boundary effects are important in (A)CIGS solar cells. It is likely that a redistribution of the absorber elements near the surface region may occur during the alkali PDT and some works show interface formation in CIGS solar cells subjected to a metal fluoride post deposition treatment [4].

In this work we employed hard X-ray photoelectron spectroscopy (HAXPES) to study the interface between CdS buffers and PDT-ACIGS absorbers, which have been exposed to different metal fluoride PDT. Two different alkali PDT are compared, RbF and CsF, to investigate how the choice of the metal fluoride treatment affects the buffer/absorber interface. In particular, the chemical and electronic properties of CdS/ACIGS interfaces in terms of intermixing, energy band alignment and composition for a set of device relevant samples have been studied.

The results show that the electronic structure at the CdS/ACIGS interface does not change for the different PDTs. However, the ACIGS composition at the near surface region seems to change depending on the applied PDT process. Possible reasons for this will be discussed. The results give insights into how selective alkali PDT could change the ACIGS surface composition, which may influence the solar cell behavior.

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LS-Contributed On Demand-7 Surface Action Spectroscopy With Inert Gas Messenger Atoms*, **Hans-Joachim Freund,*** Fritz Haber Institute of the Max Planck Society, Germany

Action spectroscopy is well established in the field of cluster physics and chemistry, where sample densities are very low. The action spectroscopy approach is based on the idea, that messenger species are attached to the object under investigation, and that laser light of varying frequency in the infrared is used to detach the messengers, which are detected with a mass-spectrometer. By varying the infrared frequency, one is able to record the vibrational spectrum of the object under study without having to record a reference spectrum. It has not been applied to surfaces due to the need for high intensity frequency variable laser sources. On the other hand, desorption induced by electronic transition as well as photo-desorption are well established fields surface science. We have over the last few years developed surface action spectroscopy employing the Free Electron Laser installed at the Fritz-Haber Institute. In the presentation I report on the conceptual design and some first results on surface vibrational spectroscopy using the approach (1-3), as well as the pros and cons of the techniques in comparison to other vibrational spectroscopy techniques.

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LS-Contributed On Demand-13 X-ray Magnetic Linear Dichroism Studies of Electrical Switching of Antiferromagnetic Order in α-Fe2O3 Epitaxial Films*, **Egecan Cogulu,*** N. Statuto,* New York University*; Y. Cheng,* Department of Physics, Ohio State University*; S. Yu, F. Yang,* Ohio State University*; R. Chopdekar, H. Ohldag,* Advanced Light Source, Lawrence Berkeley National Laboratories*; A. Kent,* New York University

Recently manipulation of antiferromagnetic (AFM) order has been gaining the attention of the spintronics community. Magnetic switching has been reported in AFM thin films based on electronic transport methods, which provide only spatially averaged information on AFM states. Other techniques, such as x-ray magnetic linear dichroism (XMLD), can provide local information on AFM domains. In this study, we report direct observation of spin reorientation in response to current pulses in (0001) α-Fe_2O_3/Pt heterostructures. Our experiment combines the application of current pulses and spatially resolved photoemission electron microscopy (PEEM) with X-ray magnetic linear dichroism to detect antiferromagnetic contrast. Pulses were applied in two different configurations A and B (Fig. 1a), and XMLD images were interleaved with current pulse sequences to reveal changes in the AFM domains (Fig. 1c). Our analysis shows that electrical pulses do not only reorient the Néel vector within the easy plane as previous work indicates. Instead, we conclude that most of the change current induced change associated with the Néel vector is a rotation out of the film plane, and different pulse directions can bring the AFM order in and out of plane deterministically.

This work is supported in part by Air Force Office of Scientific Research under Grant FA9550- 19-1-0307.

LS-Contributed On Demand-16 Probing Interfacial Ferromagnetism in Oxide Superlattices Using Depth Resolved X-Ray Spectroscopic and Scattering Techniques*, **Jay Paudel,*** Temple University*; M. Terilli,* Rutgers University*; I. Vobornik, P. Orgiani, G. Panaccione,* CNR-IOM, TASC Laboratory, Italy*; C. Klewe, P. Shafer,* Advanced Light Source, LBNL*; V. Strocov,* Swiss Light Source, PSI, Switzerland*; J. Chakhalian,* Rutgers University*; A. Gray,* Temple University

The origins of emergent interfacial ferromagnetism in $CaMnO_3$/$CaRuO_3$ and $CaMnO_3$/$LaNiO_3$ heterostructures have been investigated for nearly two decades [1-4]. Several experimental and theoretical studies suggest that this phenomenon is stabilized by charge transfer across the interface and suggest different thicknesses of the resultant ferromagnetic layers. In this comprehensive study, we have carried out polarization-dependent x-ray absorption spectroscopy and x-ray resonant magnetic scattering to probe the depth-resolved magnetic profile at the interfaces in these material systems. Furthermore, we have utilized bulk-sensitive hard x-ray photoemission spectroscopy and soft x-ray standing-wave photoemission spectroscopy in both first- and second-order Bragg geometries to probe the depth-dependent chemical profile and interfacial charge reconstruction in $CaMnO_3$. Finally, high-resolution angle-resolved photoemission spectroscopy with in-situ pulsed-laser deposition synthesis were used to track the topology of the Fermi surface of $LaNiO_3$ in the superlattice across the thickness-dependent metal-insulator transition. The results were compared to the 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

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New Trends in Structural Electronic Characterization of Materials, Interfaces, and Surfaces Using Synchrotron and FEL Based Light Sources Focus Topic

Room On Demand - Session LS-Invited On Demand

New Trends in Structural Electronic Characterization of Materials, Interfaces, and Surfaces Using Synchrotron and FEL Based Radiation Sources Invited On Demand Session

LS-Invited On Demand-1 Soft X-ray Resonant Inelastic Scattering (RIXS) to Study the Magnetic and Electronic Properties of Materials*, Nicholas Brookes,* ESRF, France **INVITED**

Soft x-ray resonant inelastic x-ray scattering (RIXS) spectroscopy has made many advances in the past few years mainly due to improved experimental facilities at third generation synchrotron sources [1].

In this talk the technique will be introduced and the current possibilities offered by soft x-ray RIXS will be demonstrated using results from the ESRF. In particular, some of the work on transition metal oxides like the nickelates [2,3], the cuprates [4] and iron [5] will be highlighted.

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LS-Invited On Demand-7 Bulk and Interface Hard-X-ray Bandmapping with Spin Resolution Combining Full-field Momentum Imaging with ToF-recording*, Gerd Schönhense,* Johannes Gutenberg University of Mainz, Germany **INVITED**

Photoelectron momentum microscopy (MM) is an alternative approach for ARPES, combining full-field k-space imaging with hemispherical or time-of-flight (ToF) energy analyzers. The heart of ToF-MM is a fast delay-line detector (DLD), recording position and time t of each counting event (at rates up to ~5x10^6 cps). 3D (k_x,k_y,t)-recording is advantageous in low-intensity experiments with soft or hard X-rays, spin mapping, or time-resolved ARPES at FEL sources. This contribution gives an overview with examples and an outlook on ongoing developments.

MM with X-ray excitation gives access to 4D bulk spectral functions $\rho(E_B,\mathbf{k})$, yielding bands, Fermi surfaces and -velocity distributions [1]. The band structure is captured in a tomographic-like mode via direct transitions to a final-state sphere, whose k-radius is tuned via the photon energy. PETRA III (Hamburg) provides 50ps photon pulses with 192ns period (40-bunch mode) at beamlines P04 (hv=300-1700eV; resolving power >10^4) and P22 (2300-7500eV; r. p. up to 10^5 with Si(333) monochromator). Information depths of 10-20nm allow studying buried structures like a 2D e-gas at an inner interface or bulk bands of a Heusler compound capped with 2nm MgO or 1nm Au.

Imaging spin filters are powerful tools complementing MM [2]; the effective figure-of-merit increases when exploiting ToF as third “coordinate” [3]. Using circ.-pol. soft X-rays, we uncovered a relation between the *Fano* spin component (along the photon helicity), the perpendicular spin component (oriented like spin in *Mott* scattering) and the circular dichroism [4]. Hard X-ray spin-MM allowed quantifying the spin gap in the half-metallic Heusler ferromagnet Co_2MnSi and the degree of (bulk) spin polarization close to E_F in magnetite, being controversially discussed for decades.

First experiments at FLASH (DESY, Hamburg) suggest a large potential of ToF-MM for fs pump-probe photoemission [5]. Event coordinates (E_B,**k**), arrival time and intensity of the corresponding FEL pulse, delay and parameters of the pump pulse are streamed in real-time and sorted into a multidimensional histogram memory. Current technical improvements concern a new objective lens without extractor field, correction and suppression of space-charge shifts, and a novel *dispersive-plus-ToF* hybrid MM. A drift section and fast DLD (<80ps time res.) behind a large single hemisphere will facilitate ToF at synchrotrons with 500MHz multibunch filling.

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LS-Invited On Demand-13 My Adventures with Synchrotrons: From Discovering New Types of Magnetism to Helping NASA*, Mikel Holcomb,* West Virginia University, USA **INVITED**

In many areas of science and the world, competition is seen as an opportunity to obtain improved performance or results. Utilizing many techniques (bulk magnetometry, neutron reflectometry and resonant x-ray magnetic scattering), we have discovered and explored the existence of competing magnetic phases in many single layer thin films that results in giant negative magnetization. We have focused on the system of complex oxide $La_{0.7}Sr_{0.3}MnO_3$. While transmission electron microscopy images show pristine epitaxial growth, the data supports that there are regions of different magnetic order. This results in interesting magnetic measurements, that share similarities with ferrimagnets with competing magnetic lattices. This competition results in spontaneous negative magnetization that aligns counter to a small applied magnetic field and inverted hysteresis loops near room temperature. This behavior has much in common with superparamagnetic nanoparticles. In this talk, the time, field and temperature dependence of these samples will be discussed to help understand this phenomenon. The switch from negative to positive magnetization effectively doubles the change in magnetization, important for some types of devices. We acknowledge funding support from NSF (DMR-1608656) for growth and optimization and DOE (DE-SC0016176) for the magnetic characterization of our films.

LS-Invited On Demand-19 Extending Time-Resolved X-Ray Diffraction using Coherence*, Mark Sutton,* McGill University, Canada **INVITED**

The use of x-ray diffraction for in-situ or in-operando measurements is now relatively common. It generally combines the power of x-ray structural measurements with x-ray's penetrating abilities to be able to perform other experimental techniques in combination. This allows one to observe how the atomic structure is or is not coupled to other material properties or underlies the processing of the material. Small angle x-ray scattering is often used, but when there is predominately crystalline order, wide angle x-ray scattering provides more detailed information. Often a trade off between better time-resolution and lower structural resolution is made to study the fastest processes. Over the last several years coherence has begun to play an important role in x-ray diffraction. Techniques like x-ray correlation spectroscopy (XPCS) and coherent diffraction imaging (CDI) being primary examples and the trade-off between the two techniques is similar to the trade-off between higher time resolution and higher structural resolution. In this talk I will explore information that is available from speckle patterns that is beyond conventional XPCS but is not as complete as CDI.

Magnetic Interfaces and Nanostructures Division

Room On Demand - Session MI-Contributed On Demand

Magnetic Interfaces Contributed On Demand Session

MI-Contributed On Demand-1 Direct Imaging of the Ac Component of the Pumped Spin Polarization With Element Specificity*, Santa Pile, T. Schaffers,* Johannes Kepler University Linz, Austria*; S. Stienen,* Helmholtz-Zentrum Dresden-Rossendorf, Germany*; M. Buchner,* Johannes Kepler University Linz, Austria*; S. Wintz,* Max Planck Institute for Intelligent Systems, Germany*; S. Mayr,* Paul Scherrer Institute, Switzerland*; J. Förster,* Max Planck Institute for Intelligent Systems, Germany*; V. Ney,* Johannes Kepler University Linz, Austria*; R. Narkowicz, K. Lenz,* Helmholtz-Zentrum Dresden-Rossendorf, Germany*; M. Weigand,* Helmholtz-Zentrum Berlin, Germany*; H. Ohldag,* Stanford Synchrotron Radiation Laboratory; University of California Santa Cruz*; J. Lindner,* Helmholtz-Zentrum Dresden-Rossendorf, Germany*; A. Ney,* Johannes Kepler University Linz, Austria

For the development of novel spintronic devices, it is important to understand the dynamic magnetic processes on the micro- and nanoscale [1]. In spintronics the generation and manipulation of pure spin currents is in the focus of research activities. Amongst the utilized fundamental effects is spin pumping where a precessing magnetization of a ferromagnet being at ferromagnetic resonance (FMR) transfers angular momentum to an adjacent nonferromagnetic layer [2], i.e. spin current. By using lithographically fabricated micro-resonators it is possible to measure FMR of the small samples with a detection sensitivity of down to 10^6 spins [3]. These micro-resonators allow combining STXM with XMCD spectroscopy and FMR (STXM-FMR). The STXM-FMR setup enables the visualization of the high frequency magnetization dynamics in the GHz regime with a high lateral resolution of nominally 35 nm and a time resolution of 17.4 ps [4]. In this contribution we present the STXM-FMR results for thin magnetic Py

($Ni_{80}Fe_{20}$) microstrips with the lateral dimensions: 5x1 μm^2 measured individually and adjacently to the Co-doped ZnO thin film.

Two types of samples were investigated: single Py microstrips and a heterostructure consisting of Co-doped ZnO thin film with the Py microstrip placed on top (Co:ZnO/Py) in order to investigate the ac component of the pumped spin polarization directly inside the nonferromagnet with ultimate spatio-temporal resolution and elemental selectivity. For FMR and STXM-FMR measurements a static magnetic field was applied in the plane of the strips. Both FMR and STXM-FMR measurements confirm that quasi-uniform and spin-wave modes can be excited in the Py microstrips. The results for the single Py strip show, that with increasing the static magnetic field it is possible to observe the transition from one mode to another and additionally observe superposition of the modes in-between the FMR signals. When superposition of the modes occurs, a non-standing character of the spin-waves can be observed for the Py strip. For the Co:ZnO/Py sample we demonstrate the feasibility to investigate the lateral distribution of the pumped ac spin polarization inside the adjacent non-ferromagnet, when Py microstrip is driven into quasi-uniform main FMR excitation or a spin-wave excitation [5].

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MI-Contributed On Demand-4 Breaking Time-Reversal Symmetry at the M Point: Spin Signal from a Surface State on Tl/Ge(111)*, **Markus Donath**, P. Eickholt, P. Krüger, S. Stolwijk, A. Schmidt,* Westfälische Wilhelms-Universität Münster, Germany

We report on an additional effect influencing the observed spin polarization in SARPES (spin- and angle-resolved photoemission) and SRIPE (spin-resolved inverse photoemission) experiments. We detected and analyzed a spin-dependent intensity asymmetry for spin-degenerate surface states at the M point in the unoccupied electronic structure of Tl/Ge(111)-(1x1) [1]. Approximating the initial state by a plane wave, we calculated the SRIPE process and obtained good agreement with the experimental data [2]. Our model reveals that this spin asymmetry at a point of time-reversal invariant momentum (TRIM) is of different origin than other effects discussed in the literature, which are based on the light detection geometry, photon energy, and experimental probing depth of the electrons. Instead, the spin asymmetry in this nonmagnetic material with spin-orbit interaction is caused by breaking the initial-state time-reversal symmetry in the experiment. Since SARPES and SRIPE are based on time-reversed processes, the effect is also expected for SARPES experiments where the outgoing photoelectrons break the time-reversal symmetry in the same way as the incoming electrons in SRIPE experiments. Understanding and considering such experimentally induced spin asymmetries is essential for correctly interpreting spin-resolved (inverse) photoemission data.

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MI-Contributed On Demand-7 Spin-orbit-induced effects in VLEED experiments from MoS_2/Au(111)*, **Christoph Angrick**, A. Henriksen, N. Mutzke, A. Reimann,* University of Münster, Germany*; M. Ewert, L. Buß,* Brandenburg University of Technology Cottbus-Senftenberg, Germany*; J. Falta,* University of Bremen, Germany*; J. Flege,* Brandenburg University of Technology Cottbus-Senftenberg, Germany*; M. Donath,* University of Münster, Germany

The influence of spin-orbit interaction on low-energy electron reflection from MoS_2 on Au(111) was studied by VLEED (very-low-energy electron diffraction) [1,2,3]. Maps of the electron reflectivity and the spin asymmetry of the reflected electron intensities were measured for a wide range of electron incidence angles and kinetic energies. To account for an adlayer coverage of about 30%, maps of the Au(111) substrate and for a MoS_2 bulk sample were measured as well. The adlayer and substrate signals were distinguished by a comparison of the maps.

For MoS_2/Au(111), we obtained a spin asymmetry of the reflected intensities, which shows a characteristic feature with alternating sign in the energy region of a VLEED fine structure [1]. The Au(111) substrate, in contrast, shows qualitatively different spin-asymmetry features, partially with reversed sign compared with MoS_2/Au(111). The results of bulk MoS_2 resemble the single-layer data to a great extend. The influence of the substrate on the results will be discussed.

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MI-Contributed On Demand-10 Direct Observation of Spin Accumulation in Cu Induced by Spin Pumping*, J. Ding,* Argonne National Laboratory*; W. Zhang,* Oakland University*; B. Jungfleisch, J. Pearson,* Argonne National Laboratory*; **Hendrik Ohldag**,* Lawrence Berkeley Lab, University of California, Berkeley*; V. Novosad,* Argonne National Laboratory*; A. Hoffmann,* University of Illinois at Urbana Champaign

Pure spin currents have been ubiquitous in contemporary spintronics research. Despite its pro-found physical and technological significance, the detection of pure spin current has largely remained indirect, which is usually achieved by probing spin-transfer torque effects or spin-to-charge conversions. By using scanning transmission X-ray microscopy, we report the direct detection and spatial mapping of spin accumulation in a nonmagnetic Cu layer without any direct charge current injection. Such a pure spin current is induced by spin pumping from a $Ni_{80}Fe_{20}$ layer and is not accompanied by concomitant charge motion. The observed frequency dependence indicates that the signal is dominated by a coherent, pure spin current, but the magnitude of the spin accumulation suggests also possible additional thermal contributions. Our technique takes advantage of the X-ray magnetic circular dichroism and the synchronization of microwave with X-ray pulses, which together provide a high sensitivity for probing transient magnetic moment. From the detected X-ray signals, we observe two distinct resonance modes induced by spin pumping, Based on micromagnetic simulations, we attribute these two resonances to non-linear microwave excitations. Our result provides a new pathway for detecting pure spin currents that originate from many spintronics phenomena, such as spin Hall and spin Seebeck effects, and which can be applied to both metal and insulator spin current sources [1].

Work at Argonne, including experimental design and measurement, sample fabrication, data analysis, and manuscript preparation, was supported by the U.S. Department of Energy (DOE), Office of Science, Basic Energy Sciences, Materials Science and Engineering Division under Contract No. DE-AC02-06CH11357. Use of the Stanford Synchrotron Radiation Light source, SLAC National Accelerator Laboratory, is supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Contract No. DE-AC02-76SF00515. W.Z. acknowledges the DOE visiting FacultyProgram.

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MI-Contributed On Demand-13 Spatially Resolved Ferromagnetic Resonance of a Single Fe_3O_4 Nanoparticle Chain Using Scanning Transmission X-Ray Microscopy*, **Thomas Feggeler**, B. Zingsem, R. Meckenstock,* University of Duisburg-Essen, Germany*; H. Ohldag,* Lawrence Berkeley National Laboratory (LBNL)*; M. Farle, H. Wende, K. Ollefs,* University of Duisburg-Essen, Germany

Scanning Transmission X-Ray Microscopy imaged Ferromagnetic Resonance (STXM-FMR) [1, 2] at the Fe L_3-edge was used for the first-time detection of the magnetization dynamics of a bi-segmented chain of 19 Fe_3O_4 nanoparticles (particle diameter: 40-50 nm), naturally grown inside a bacterium Magnetospirillum Magnetotacticum MS-1. A uniform resonant excitation within the chain segments was measured element specifically with a spatial resolution of about 50 nm and pico second time resolution. Micromagnetic simulations of a corresponding nano particle chain agree well to the observations made in the experiment. The combination of conventional Ferromagnetic Resonance, micromagnetic simulations and STXM-FMR allows the comprehensive characterization of magnetization dynamics on the nanoscale, necessary for the development of genetically engineered spin wave computing devices, as suggested in [3].

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Helpful discussions with A. Ney and his team are acknowledged.

MI-Contributed On Demand-16 Scanning NV Magnetometry for Semiconductor Device Analysis*, U. Celano,* IMEC, Belgium*; **Peter Rickhaus**, H. Zhong,* Qnami AG, Switzerland*; F. Ciubotaru,* IMEC, Belgium*; L. Stoleriu,* Alexandru Ioan Cuza University, Romania*; A. Stark, F. Favaro de Oliveira, M. Munsch,* Qnami AG, Switzerland*; P. Favia, M. Korytov, P. Van Marcke,* IMEC, Belgium*; P. Maletinsky,* Qnami AG, Switzerland*; C. Adelmann, P. van der Heide ,* IMEC, Belgium

Scanning NV magnetometry (SNVM) is an emerging quantum sensing technique which allows to measure minute magnetic fields with nanoscale resolution. We present a specific use-case of SNVM: the characterization of magnetic nanowires. Magnetic nanowires are among the essential building-blocks of contemporary spintronic devices since their magnetic properties can be tuned by their geometry, and their fabrication is compatible with standard semiconductor fabrication schemes. While their topography and homogeneity can be well characterized with established techniques, it remains difficult to access their microscopic *magnetic* properties which are key to improve device performance.

Here, we demonstrate magnetic imaging of ultra-scaled magnetic nanowires by SNVM. The imaging reveals the presence of weak magnetic inhomogeneities inside in-plane magnetized nanowires that are largely undetectable with standard metrology. In this context, we will discuss the potential of SNVM for semiconductor device analysis.

MI-Contributed On Demand-19 $Co_2Fe_{1.25}Ge_{0.75}$: Single-Phase, Highest Magnetic Moment, Highest Curie Temperature*, **Shambhu KC**, R. Mahat,* The University of Alabama*; S. Regmi,* University of Alabama*; J. Law,* The University of Alabama*; V. Franco,* Universidad de Sevilla, Spain*; G. Mankey, W. Butler, A. Gupta, P. LeClair,* The University of Alabama

Spintronic device performance is compromised when thermal effects impact magnetic properties and spin polarization of the materials [1]. One way of mitigating this problem is to find materials having a very high saturation moment (MS) and high Curie temperature (TC). The full Heusler alloy Co2FeGe theoretically has promise to meet this demand. However, its inability to form a single-phase compound makes it problematic for application. The addition of a fourth element is sometimes useful in stabilizing a single-phase compound [2], but it can be detrimental to some properties, particularly due to the increased probability of chemical disorder. In this talk, we present the successful synthesis of a single-phase compound based on Co2FeGe, viz Co2Fe1.25Ge0.75, by altering the stoichiometry rather than adding a fourth element. For the single-phase compound, MS as high as 6.7 ± 0.1 μB/f.u. at 5K and a Curie temperature of 1135 ± 5 K are measured – to our knowledge the highest reported for full Heusler alloys. In addition, thin films of Co2Fe1.25Ge0.75 deposited on Al2O3(110) and MgAl2O4(100) substrates are highly epitaxial. The structural quality of the films can be argued to be among the best reported for Heusler films to date. The thin film MS values also agree with the bulk MS. First principle calculations suggest the system exhibits total energy minimum at the experimental lattice parameter. These calculations also predict an enhancement in magnetization with a value closer to the experimental value. Hence, the highest moment, highest Curie temperature, and the ability to grow excellent quality single crystal films make Co2Fe1.25Ge0.75 a strong candidate for many device applications.

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MI-Contributed On Demand-22 Defects in Magnetic Weyl Semimetal $Co_3Sn_2S_2$*, **Zheng Gai**, Q. Zou, M. Fu, L. Zhang,* Oak Ridge National Laboratory*; R. Xue,* University of Tennessee Knoxville*; J. Yan,* Oak Ridge National Laboratory*; M. David,* University of Tennessee Knoxville*; M. Yoon,* Oak Ridge National Laboratory, USA

Co3Sn2S2 is a magnetic Weyl semimetal with kagome-lattice. In such samples, the existence of bulk Weyl nodes, which are formed under broken inversion or time-reversal symmetry, creates nontrivial topological properties like robust Giant anomalous hall effect. The surface–bulk correspondence ensures the bulk bands related topological “Fermi arc” surface bands dispersion. In this presentation, we use low temperature high magnetic field scanning tunneling microscope, spin polarized STM, and quasiparticle interference (QPI) to study the influence of local defects to the Weyl nodes movement, including magnetic and nonmagnetic vacancies and adatoms. S, Co and Sn vacancies and adatoms are identified, their behavior under magnetic field are studied. The interplay among topology, defects and magnetism are discussed for the understanding of the involved quantum phenomena.

This research was conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.

MI-Contributed On Demand-25 Optimizing Magneto-Elastic Coupling in Multilayer Fega/NiFe Thin Films for Magneto-electric Applications*, **Adrian Acosta**, J. Chang,* UCLA

Magnetoelectric (ME) materials provide the ability to efficiently control magnetism with electric fields, offering the potential to circumvent the size and efficiency limitations of traditional electronic devices. One barrier towards enhancing the efficiency in ME devices is the need for ferromagnetic materials that exhibit both a large magnetostriction and soft magnetic properties to yield a high magneto-elastic coupling. Additionally, for microwave ME applications, a low Gilbert damping is needed for low loss operation whereas materials with large magnetostriction typically exhibit high Gilbert damping coefficients due to their large spin lattice coupling (α ~ 0.2 vs ~ 0.03 for most ferromagnetic metals).

FeGa is a material of interest due to its large magnetostriction (~275 ppm in polycrystalline bulk) and large piezomagnetic coefficient (>2 ppm/Oe) but is highly lossy at high frequencies and exhibits a large magnetic hysteresis. Recent studies of FeGa/NiFe (1:1 volume fraction) multilayer (ML) thin films [1-2] have found that these nanolaminates can achieve a low coercivity (<10 Oe) and can reach a >4x increase in magnetoelectric coefficient compared to single phase FeGa films. However, prior work on FeCo/NiFe suggests that only a thin interlayer of NiFe is required to achieve a significant enhancement in soft magnetic properties [3]. In this work, we explore a multilayering strategy of FeGa with NiFe – (100 nm FeGa / N)/ (2.5 nm NiFe) – where N represents the total number of bilayers. It was found that 2 bilayers optimized the lowest in-plane coercivity (7 Oe) and Gilbert damping coefficient (0.014). Compared to multilayers with an insulating layer insertion, this is less than an order of magnitude lower than reported FeGaB(25 nm)/Al2O3/FeGaB(25 nm) (α = 0.24) [4] and within the same order of magnitude for MLs we have previously studied of FeGa(10 nm)/NiFe(10 nm)/FeGa(10nm) with an Al2O3 insertion (α = 0.006).

Furthermore, it is expected that the magnetostriction increases linearly with the number of bilayers as the contribution from interfacial magnetostriction also increases. XRD and AFM imaging are used to correlate the coercivity, gilbert damping, and magnetostriction with the grain size and surface roughness of the composite film with increasing number of bilayers. This ML strategy shown here can be used to help design materials with a higher magneto-elastic coefficient for strain-mediated magnetoelectric devices.

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MI-Contributed On Demand-28 Large Temperature Dependent Spin Torque Efficiency in Antiferromagnetic FeRh*, **Jonathan Gibbons**,* University of Illinois at Urbana Champaign*; T. Dohi,* Tohoku University, Japan*; H. Saglam,* Yale University*; J. Pearson,* Materials Science Division, Argonne National Laboratory*; S. Fukami,* Tohoku University, Japan*; A. Hoffmann,* University of Illinois at Urbana Champaign

Magnetic ordering is an attractive trait in spin source materials for spintronics applications, as this ordering can break the material's symmetry and allow for ordinarily forbidden exotic spin torques ideal for efficiently controlling perpendicularly magnetized nanomagnets or driving spin torque oscillators for energy-efficient neuromorphic computing. In ferromagnetic materials, controlling the magnetic ordering direction can control the spin polarization of the generated spin currents. Iron rhodium (FeRh) exhibits a transition between a low-temperature antiferromagnetic (AFM) state and a high-temperature ferromagnetic (FM) state. For appropriate growth parameters, this transition can be found close to 300K, such that both the FM and AFM states are stable at room temperature, making it an ideal material for probing the influence of magnetic ordering on spin geometry. We investigate the influence of magnetic ordering and present measurements of the spin torque efficiency in iron rhodium over a range of temperatures, and report large exotic spin torques in anti-ferromagnetic FeRh that grow significantly as the temperature is varied, and consider the possible influence of magnetic ordering on these findings.

This work was supported as part of Quantum Materials for Energy Efficient Neuromorphic Computing, an Energy Frontier Research Center funded by the U.S. DOE, Office of Science.

MI-Contributed On Demand-31 Effect of Sn Doping on Surface States of Bi_2Se_3 Thin Films*, Jennifer DeMell,* *G. Stephen,* Laboratory for Physical Sciences*; I. Naumov,* Howard University*; S. Tyagi,* University of Maryland, College Park*; O. Vail,* Army Research Laboratory*; M. Dreyer,* University of Maryland, College Park*; R. Butera, A. Hanbicki,* Laboratory for Physical Sciences*; P. Taylor,* Army Research Laboratory*; I. Mayergoyz,* University of Maryland, College Park*; P. Dev,* Howard University*; A. Friedman,* Laboratory for Physical Sciences

Bi_2Se_3, widely studied as a topological insulator, has great potential for applications in low-power electronics and quantum computing. Intrinsic doping, however, presents a persistent challenge, leading to predominantly bulk conduction. In this work, we use substitutional Sn dopants to control the Fermi level in Bi_2Se_3 films. Scanning tunneling microscopy (STM) shows a shift in the local density of states toward the Dirac point as more Sn is incorporated. Density functional theory calculations elucidate the STM results, showing that Sn adds metallic states near the Fermi level that are localized to the defect sites while leaving the Dirac cone undisturbed. Electronic transport measurements demonstrate that the Sn defects increase the separation between bulk and surface states, though bulk conduction remains a dominant component.

MI-Contributed On Demand-34 Control of Domain Wall Patterning and Anomalous Response Functions in Ferrimagnetic Spinels*, Lazar Kish,* University of Illinois at Urbana-Champaign*; A. Thaler,* Oak Ridge National Laboratory*; M. Lee,* Los Alamos National Laboratory*; A. Zakrzewski,* University of Illinois at Urbana-Champaign*; D. Reig-i-Plessis,* University of British Columbia, Canada*; B. Wolin, X. Wang,* University of Illinois at Urbana-Champaign*; K. Littrell,* Oak Ridge Natinal Laboratory*; R. Budakian,* University of Waterloo, Canada*; H. Zhou,* University of Tennessee Knoxville*; Z. Gai, M. Frontzek,* Oak Ridge National Laboratory*; V. Zapf,* Los Alamos National Laboratory*; A. Aczel, L. DeBeer-Schmitt,* Oak Ridge National Laboratory*; G. MacDougall,* University of Illinois at Urbana-Champaign

The ferrimagnetic spinels are known for anomalous magnetoresponsive behaviors which stem from strong spin-lattice coupling and orbital ordering effects. Single crystals of these materials (Mn3O4, MnV2O4, FeV2O4) display a nanometer length-scale patterning of magnetostructural domains which is strongly correlated with these effects. The domain patterns are remarkably sensitive to environmental stress and controllable by applied magnetic fields. In this talk, we present reciprocal-space characterizations of these mesoscale patterns using small-angle neutron scattering, which allows us to correlate various response functions including inverse magnetoelastic effect and magnetodielectric effects with the onset and field response of domains. Meanwhile, neutron diffraction and small-angle X-ray scattering reveal a strong intertwining of these effects with lattice degrees of freedom, collectively establishing strain as an important tuning parameter for anomalous behavior in these materials.

MI-Contributed On Demand-37 Anomalous Hall Effect in Heterostructures Based on $MnBi_2Te_4$ Grown by MBE*, Seul-Ki Bac,* *L. Riney, J. Wang,* University of Notre Dame*; K. Koller,* Saint Mary's College*; X. Liu, M. Zhukovskyi, T. Orlova, M. Dobrowolska, J. Furdyna, B. Assaf,* University of Notre Dame

The intrinsic magnetic topological insulator $MnBi_2Te_4$ provides a great platform to explore quantum phenomena, such as quantum anomalous Hall effect and axion insulators, as reported earlier. However, the search of interesting electromagnetic effects in this material was hindered by the difficulty of preparing its high-quality films with well-controlled composition and thickness. In this study, we compare three different types of Mn-Bi-Te samples grown by molecular beam epitaxy: a heterostructure of $MnBi_2Te_4$ and Bi_2Te_3, a single $MnBi_2Te_4$ layer, and a heterostructure of $MnBi_2Te_4$, Bi_2Te_3, and MnTe. We measured the anomalous Hall effect (AHE) in each case and demonstrate its evolution from a two-component AHE contain the contribution of the MnTe and $MnBi_2Te_4$, to single component AHE resulting from few-layer $MnBi_2Te_4$ scattered out in a Bi_2Te_3 matrix, and finally to an antiferromagnetic AHE, characteristic of the pure phase of $MnBi_2Te_4$. Our work provides an understanding of the AHE for all three possible heterostructure compositions and paves the way for the realization of new quantum phenomena in pure $MnBi_2Te_4$ thin films.

MI-Contributed On Demand-40 Magnetic Transition Behavior of Epitaxial $Fe_{47}Rh_{47}Pd_6$ Films*, Gary Mankey,* University of Alabama*; H. Sato,* Tohoku University, Japan*; N. Pachauri,* Intel*; S. Keshavarz,* University of Alabama*; H. Lee,* Trinity College Dublin, Ireland*; P. LeClair,* University of Alabama*; O. Mryasov,* Department of Physics and Astronomy

The structural and magnetic properties of Fe-Rh-Pd epitaxial thin films grown on MgO(001) were studied as a function of growth temperature. Films grown above 400 C exhibit a first-order antiferromagnetic to ferromagnetic magnetic phase transition with a transition temperature that decreases as the growth temperature is increased. The chemical order parameter of the Fe-Rh-Pd films is nearly independent of the growth temperature, while the lattice constants change slightly. A comparison of our structural, magnetic, and electrical transport results with first-principles-based calculations as well as literature results indicate that the transition temperature of Fe-Rh-based alloy films depends sensitively on the lattice parameters, and is of electronic origin. The transition temperature and its width can be tuned over a wide range by controlling the crystal structure via growth conditions or post-deposition annealing.

MI-Contributed On Demand-43 The Critical Role of Checkerboard Spin Fluctuations in High-Tc Single Layer Iron Chalcogenide Superconductors*, Qiang Zou,* *H. Zhang,* West Virginia University*; T. Shishidou, M. Weinert,* University of Wisconsin Milwaukee*; L. Li,* West Virginia University

Single layer FeX (X=Te, Se, S) epitaxially grown on $SrTiO_3$ (STO) substrate represents a model system for probing a host of quantum phenomena due to the interplay of topology, magnetism and superconductivity.

For example, single layer FeTe exhibits long-range bi-collinear antiferromagnetic (AFM) order, which is not superconducting. We found that the AFM order, however, can be suppressed by alloying with Se at >10% concentrations, where enhanced superconductivity emerges [1]. Our spin spiral calculations further showed that the ground state is magnetically disordered paramagnetic, where local checkerboard (CB) AFM fluctuations is critical to the high Tc superconductivity in FeSe [2].

In this work, the impact of S incorporation into single layer FeSe is investigated. Our calculations indicate that the energy difference between CB and co-linear (CL) AFM order increases with increasing S. Fits of the spin-spiral dispersion to spin models leads to Heisenberg parameters J2/J1 of 0.55 for FeSe and 0.72 for FeS, placing the FeS system closer to the CL phase boundary and possibly decreasing the importance of CB fluctuations [3]. Experimentally, we synthesize high quality single layer $FeSe_{1-x}S_x$ films on STO(001) substrates by molecular beam epitaxy, and probe their electronic properties using scanning tunneling microscopy/spectroscopy and angle-resolved photoemission spectroscopy [3]. We observe that with increasing S concentration x, the Fermi surface at M point becomes more anisotropic and the effective mass decreases from 4.3 to 1.2 m_e, while the hole pocket at Γ point stays at 60 meV below the Fermi level. More importantly, no Tc enhancement is observed for films with x > 0.7. Our findings demonstrate that the CB AFM fluctuations plays an essential role in the enhanced superconductivity in epitaxial single layeriron chalcogenidesuperconductors on STO.

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MI-Contributed On Demand-46 Magnetic Anisotropy in a Single Crystal Antiferromagnetic Thin Film*, Saima Siddiqui,* University of Illinois at Urbana Champaign*; J. Pearson,* Argonne National Laboratory*; A. Hoffmann,* University of Illinois at Urbana-Champaign

Antiferromagnetic materials promise to show magnetization dynamics, including switching, at ultra-high frequency and thus are of immense interest for next generation memory and logic applications. Besides, spin waves in an antiferromagnetic insulators propagate very efficiently. However, electrically reading the states of the antiferromagnetic materials is not easy. Recently, spin Hall magnetoresistance (SMR) has been identified as one of the promising ways to access the surface states of the antiferromagnetic insulators. In this work, we focus on α-Fe_2O_3 insulator. We grow a 200-nm thick α-Fe_2O_3 film on (11-20) Al_2O_3 by reactive sputtering at 5 mTorr. A 6-nm thick Pt film is deposited in-situ on the Fe_2O_3 film. We measure the SMR of the patterned Hall bar structure of Pt at low temperatures and room temperatures. Below the Morin transition, we observe positive and negative magnetoresistance in the Pt/Fe_2O_3 bilayers depending on the direction of the current flow at the spin flop transition. This identifies that SMR can clearly determine the anisotropy of a thin film antiferromagnetic insulator. Moreover, we observe the spin-flop field of α-Fe_2O_3 using the Hall measurement in addition to the SMR measurement. The Hall magnetoresistance is 100x higher than the SMR at the spin-flop field. We will show a detailed study of the dependence of magnetoresistance on angular fields at different temperatures. Our study reveals important physical phenomena in the antiferromagnetic Fe_2O_3 thin film, which in turn will help to design energy efficient antiferromagnetic devices.

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Magnetic Interfaces and Nanostructures Division
Room On Demand - Session MI-Invited On Demand
Magnetic Interfaces Invited On Demand Session

MI-Invited On Demand-1 From Spin Spirals to Spin Glasses - Imaging Complex Magnetism on the Atomic Scale*, Daniel Wegner,* Radboud University, Nijmegen, Netherlands **INVITED**

I will present recent developments and discoveries in atomically resolved magnetic microscopy based on scanning probes (SPM). (a) A novel method we call SPEX microscopy combines spin-polarized scanning tunneling microscopy (SP-STM) with magnetic exchange force microscopy (MExFM), and enables the disentanglement of structural, electronic and magnetic contributions to the SPM signal [1]. This way, we were able to resolve the antiferromagnetic chiral spin spiral structure of a Mn monolayer on W(110) with unprecedented resolution [2]. (b) Our recent development of a dilution-fridge UHV SP-STM allows for the interrogation of in situ MBE-grown magnetic samples down to a temperature of 30 mK and in fields up to 9 T [3].

As a showcase, I will present the first atomic-scale magnetic microscopy results on the surface of the rare-earth element neodymium (Nd), whose complex magnetic ground state is still under debate after more than half a century of experiments. We surprisingly found evidence that Nd manifests the first example of a recently predicted new state of matter referred to as self-induced spin glass [4]. Contrary to the accepted paradigm that a spin glass requires structural disorder (as found in dilute magnetic alloys), self-induced glassiness can also occur in defect-free single crystalline materials. SP-STM experiments on extremely clean MBE-grown Nd(0001) films on W(110), combined with *abinitio* calculations and atomistic spin-dynamics simulations, reveal very complex non-collinear spin structures with local but no long-range order. By performing measurements at various temperatures (30 mK - 7 K) and as a function of magnetic field, we observed and quantified the aging phenomenon, which distinguishes spin glasses from quantum spin liquids or spin ice. We relate the glassy behavior to the crystalline symmetry, leading to competing magnetic interactions. This not only resolves the long-standing debate on the magnetic ground state of neodymium, but suggests that glassiness may arise in elemental solids without disorder if certain symmetry conditions are met.

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MI-Invited On Demand-7 Magnetic Exchange and Anisotropy in Perpendicular Magnetic Tunnel Junction Nanopillars: Experiment and Micromagnetic Modeling*, Jamileh Beik Mohamadi,* Loyola University New Orleans*; A. Kent,* New York University **INVITED**

Perpendicular magnetic tunnel junctions, pMTJs, are extensively used in industry for sensing and data storage applications. pMTJs are multilayered structures composed of several ferromagnetic and non-magnetic thin films, including a free layer with switchable magnetization. Reducing the dimensions of pMTJs, including the thickness of layers and the lateral size, is desirable to enhance the energy efficiency, speed, and data storage density. As the dimensions, mainly the thickness, of the magnetic film decrease, interfacial effects dominate, and the magnetic properties change. Of particular interest are the interfacial perpendicular magnetic anisotropy, PMA, and the exchange interaction of the pMTJ free layer that serves as write media. The reason is: 1) strong PMA is needed to obtain higher thermal stability of the device, and 2) exchange interactions set the length scale for micromagnetic inhomogeneities. Therefore, they both have a significant effect on the spin torque switching dynamics and the switching time[1, 2].

Interfacial anisotropy of the free layer drops inversely with its thickness. This implies that any spatial inhomogeneities of the film thickness alter the magnetic energy landscape, such as in the form of a higher-order perpendicular anisotropy. Moreover, the magnetic exchange interaction (Heisenberg model) of the free layer thin film is reduced significantly compared to bulk values. We have observed this effect when we used VSM analysis used to determine the exchange constant of CoFeB thin film. Exchange interaction is reduced further for a composite CoFeB/W/CoFeB free layer in pMTJ stack. This reduction of exchange energy is also observed when dynamic methods such as spin-torque ferromagnetic resonance, ST-FMR, are used.

The higher-order anisotropy and the reduced exchange interaction in the free layer thin film also have significant effects on the spin-torque switching dynamics of the free layer. On the one hand, the presence of higher-order anisotropy reduces the switching time[2]. On the other hand, the reduced exchange interaction results in delayed switching[3]. I will present some of the implications of the above-mentioned effects on the switching dynamics and switching speed of pMTJ free layers.

Acknowledgments

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MI-Invited On Demand-13 Utilizing Vacuum States Above Surfaces for Imaging and Manipulation of Atomic-Scale Magnetism*, Anika Schlenhoff,* University of Hamburg, Germany **INVITED**

Non-collinear spin textures in ultra-thin film systems are in the focus of ongoing research. Specifically, atomic-scale magnetic skyrmions raise expectations for their application in information technology as logic spin-electronic devices or in recording media. For their characterization and manipulation spin-sensitive techniques with ultimate spatial resolution are required. Spin-polarized scanning tunneling microscopy (SPSTM) can resolve magnetic surface structures down to the atomic-scale. However, based on spin-polarized tunneling of electrons, this imaging technique is restricted to tip-sample separations of only a few

Ångstroms, making the technique very fragile in terms of sensitivity to vibrations or for accidental, destructive tip-sample collisions. Ångstrom distances are also technically challenging for practical applications in future spin-electronic devices.

Spin-polarized vacuum resonance states (sp-RS) are unoccupied electronic states in the vacuum gap between a probe tip and a magnetic sample. As I will show in this talk, these states exhibit the same local spin quantization axis as the spin texture of the underlying sample surface, even when the spins are rotating on the atomic-scale [1]. In an SP-STM setup, the sp-RS can be addressed by spin-polarized electrons that tunnel resonantly from the magnetic tip into the surface, resulting in a magnetic image contrast governed by the spin-polarized electron tunneling into the sp-RS [1]. Our SP-STM experiments on ultrathin films with non-collinear spin textures demonstrate that this resonant tunneling allows for atomic-scale spin-sensitive imaging in real space at tip-sample distances of up to 8 nm. This technique provides a loophole from the hitherto existing dilemma of losing spatial resolution when increasing the tip-sample distance in a scanning probe setup [2]. Experimental results will be discussed in terms of the sp-RS' spin-splitting and the magnetic contrast as a function of bias and tip-sample distance, as well as in terms of the atomic-scale nature of the resonant tunneling condition between the probe tip and the sample.

The tip-sample distances demonstrated in this talk are in the range of present flying heights of read-write heads in data storage devices. In combination with thermally-assisted spin-transfer torque switching via sp-RS [3], our approach qualifies for a spin-sensitive read-write technique with ultimate lateral resolution in future spin-electronic applications.

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MI-Invited On Demand-19 Magnetism in Topological Crystalline Insulator Heterostructures*, Badih Assaf,* University of Notre Dame INVITED

Topological crystalline insulators (TCI) arise in the PbSnSe and PbSnTe material family and host valley degenerate surface states protected by mirror symmetry. The rocksalt crystal structure of these materials, and the wide tunability of their energy gap enables the realization of epitaxial heterostructures of TCIs and normal insulators, where topological interface states have been probed by magnetooptics. In this talk, I will discuss the recent growth and electrical magnetotransport characterization of heterostructures of TCI(Pb0.7Sn0.3Se)/EuSe, where the normal insulator is replaced by the magnetic insulator EuSe to obtain an interfacial Zeeman effect. Strong Shubnikov-de-Haas oscillations are observed in these structures evidencing their high carrier mobility. The oscillations coexist with the magnetism of EuSe, but further tuning of the Fermi level is likely needed to measure the impact of the Zeeman exchange on Landau levels. The realization of these heterostructures enables a direct determination of the exchange interaction energy induced by proximity, not yet measured for any topological insulator. Work supported by NSF-DMR-1905277.

MI-Invited On Demand-25 Moving Toward Antiferromagnetic Straintronics*, Michelle Jamer,* United States Naval Academy INVITED

Strain-coupled multiferroics are currently being pursued due to their enhanced tunability towards room temperature applications. [1] The artificial systems are proposed to augment intrinsic (single-phase) multiferroics, since they can be optimized for proposed systems via magnetoelectric coupling. Information storage needs are dramatically increasing and require sub 10 nm magnetic feature sizes and lower energy writing. [2] Traditional magnetic memory writing systems are plagued by large current densities for switching the magnetization, which causes the magnetic size for information storage to remain above this 10 nm magnetic feature ideal. [3]

Antiferromagnetic multiferroics are attractive or spintronic applications, since there is no external magnetic moment to interfere with surrounding components. In this talk, the systems with magnetostrictive Galfenol, Terfenol, and $Co_{1-x}Tb_x$ coupled to a piezoelectric PMN-PT will be discussed. Polarized neutron reflectometry (PNR) has been used in these systems to understand the unique reversal dynamics and the effect of voltage on the magnetization.[4] Overall, these measurements have shown that the strain-coupling could lead to the next generation of straintronic materials. Most interestingly, $Co_{1-x}Tb_x$ is a fully compensated ferrimagnetic material when x= 0.22, and has shown to have a fairly large magnetostriction, which could be the material of future straintronic devices.

Funded by NSF-DMR-1904446.

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MI-Invited On Demand-31 A Two-Dimensional Atomically-Thin Manganese Gallium Nitride Magnetic Monolayer*, Y. Ma,* Ohio University*; D. Hunt,* GIyA, CAC-CNEA and Consejo Nacional de Investigaciones Cient´ıficas y T´ecnicas - CONICET, Argentina*; K. Meng,* The Ohio State University*; T. Erickson,* Ohio University*; F. Yang,* The Ohio State University*; M. Barral, V. Ferrari,* GIyA, CAC-CNEA and Consejo Nacional de Investigaciones Cient´ıficas y T´ecnicas - CONICET, Argentina*; **Arthur R. Smith,*** Ohio University INVITED

Two-dimensional (2D) magnetic materials are of great interest for fundamental science as well as advanced applications. Besides 2D materials, the dilute magnetic semiconductors (DMS) have also captured worldwide interest by combining magnetism with electronic properties. MnGaN-2D is the ultimately-thin limit of a novel DMS material, but having a densely concentrated and well-ordered structural design. With 1/3 of the monolayer being magnetic manganese atoms, MnGaN-2D shows room-temperature ferromagnetism as demonstrated with spin-polarized scanning tunneling microscopy as a function of applied magnetic field, and as predicted by first-principles theoretical calculations which reveal the origins of the ferromagnetism through its highly spin-split and spin-polarized electronic structure.[1]

These results are backed up by SQUID magnetometry measurements which reveal a high spin-polarization of ~79% at room temperature as well as perpendicular magnetic anisotropy. But this intriguing system shows even more interesting behavior as it turns out that its electronic structure is strain-dependent leading to the possibility of magneto-elasticity. Theoretical calculations reveal a high sensitivity of the spin-polarized electronic structure to lattice strain, offering one explanation for results from tunneling spectroscopy (*dI/dV*) measurements, which reveal unexpected variations in the electronic properties.

Simulations, including both isotropic and anisotropic cases, confirm a highly strain-dependent manganese partial density of states. Spin-orbit coupling is included which indicates either *out-of-plane* perpendicular magnetic anisotropy (PMA) or *in-plane* magetic anisotropy, dependent on the type of strain whether compressive or tensile. Clear evidence for both compressive and tensile local lattice strains is found by detailed analysis of atomic resolution STM images which reveal a highly non-Gaussian lattice spacing distribution.

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MI-Invited On Demand-37 Topological Multiferroics*, Sinéad Griffin,* Lawrence Berkeley Lab, University of California, Berkeley INVITED

Multiferroic materials that combine magnetism and ferroelectricity are described by order parameters in real space under the Landau's phenomenological theory. The recent strides in topological order -- described by reciprocal space invariants -- have identified several new classes of materials including topological insulators and Weyl/Dirac semimetals. In this talk I will address the question: how can topological order in reciprocal space be combined with, and possibly controlled by, real space order parameters such as magnetism and ferroelectricty? I will identify the fundamental design rules for their coexistence in several classes of materials and give examples how topological order can be controlled via multiferroic order parameters.

MEMS and NEMS Group
Room On Demand - Session MN-Contributed On Demand
MEMS and NEMS Contributed On Demand Session

MN-Contributed On Demand-1 Observation of Tunable Opto-Mechanical Responsivity in Two-Dimensional Semiconducting Nanoelectromechanical Resonators*, Jiankai Zhu,* University of Electronic Science and Technology of China*; P. Zhang,* Shanghai Jiao Tong University, China*; J. Li, B. Xu, S. Wu, F. Xiao, Y. Liang, T. Wen, F. Wang,* University of Electronic Science and Technology of China*; R. Yang,* Shanghai Jiao Tong University, China*; Z. Wang,* University of Electronic Science and Technology of China

Introduction

Nanoelectromechanical systems (NEMS) based on two-dimensional (2D) materials typically have motional parts that are atomically-thin, with displacement in the picometer range or even smaller[1]. When measuring the nanomechanical device motion, a key challenge is to optimize the signal transduction efficiency (responsivity) in order to best detect the infinitesimal motion[2][3]. Here we demonstrate tuning of the responsivity in optically-transduced atomically-thin NEMS resonators, by controlling the device deflection and thus profiles, and demonstrate the importance of optimizing the measurement condition.

Methods

In this work, we study the tuning of opto-mechanical responsivity with laser position and gate voltage, by using a custom-built 2D NEMS resonator measurement system, including optical components for laser interferometry, a vacuum chamber to keep the device in $\sim 1\times10^{-6}$ Torr environment, an x–y stage with precise position control, and electrical connections for gate tuning and driving (Fig. 1a). The MoS_2 NEMS resonator (Fig. 1b & 1c) is fabricated using a dry transfer method[4], and actuated capacitively through its gate electrode.As the laser is incident on the device, the reflected light intensity (incident on the photodetector) varies with the position of the MoS_2 flake, resulting from optical interferometry (Fig. 2a).

Results

When DC gate voltage (V_g) is applied, the electrostatic force pulls down the MoS_2, which changes the interferometry condition and tunes the reflected light intensity. For the same MoS_2 resonator under V_g = 0.5 V and 7 V, the resonance signal amplitudes are clearly different, indicating a change in responsivity (Fig. 2). When the gate voltage varies from -10 V to 10 V, we observe the striking feature of 0 responsivity: at certain gate voltage (~ ±6V), the resonant signal becomes unmeasurable, as the responsivity crosses 0 point (Fig. 3). We confirm this is due to the change in interferometric condition and thus responsivity, by measuring the same device, under the exact same excitation amplitude and gate voltages, but at different laser spot positions. Fig. 4 clearly shows that as the laser spot moves, the interferometric condition changes due to different vacuum gap size, and the zero responsivity condition is met at different gate voltages (orange arrows). We further estimate the profile of the MoS_2 NEMS resonator using finite element simulation (Fig. 5). These results clearly demonstrate the importance of laser spot position and gate voltage on the responsivity of 2D NEMS resonators, and provide important guidelines for optimizing the transduction efficiency of resonances.

Reference

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MN-Contributed On Demand-4 Improving Signal-to-Noise Ratio and Noise Matching in AlN NEMS Resonators Using Parametric Amplification*, Tahmid Kaisar,* *J. Lee, P. X.-L. Feng,* University of Florida

Parametric amplification has been widely employed in various fields such as in optics, nano-mechanics, and electronic circuits to increase signal-to-noise ratio (SNR) of low-level signals through modulating system parameters. Due to very small mechanical motions of resonant nano/microelectromechanical systems (NEMS/MEMS), it has been challenging to have an efficient displacement signal transduction method, and displacement signals are often superposed on the much larger electrical background and noise from readout electronics. Using parametric amplification, it is possible to amplify the signal directly in the mechanical domain first, before electrical transduction, allowing us to alleviate excess amplifier noise. Parametric effects have been achieved in NEMS/MEMS by changing certain device parameter at twice the resonance frequency [1]. Besides parametric gain, it can enhance quality (Q) factors of the devices [2], improve sensitivity of atomic force microscopy (AFM), enhance SNR in gyroscopes, *etc*.

In this work, we demonstrate parametric amplification of the thermomechanical noise in an optically and piezoelectrically transduced AlN NEMS resonator, which has a two-dimensional (2D) square diaphragm with a side length of 26 mm and thickness of 140 nm. The device shows a resonance frequency of ~7 MHz and a Q factor of 8800 in the linear regime. Duffing nonlinearity and dynamic range (DR) of the device are characterized. Next, we introduce 2ω parametric pumping voltage (v_p) to the device and measure displacement of thermomechanical noise in both optical and electrical domains, simultaneously. We find that the thermomechanical noise is gradually amplified as v_p increases from 1mV to 30mV, and it goes into self-oscillation regime when $v_p \geq 25.3$mV (*i.e.*, parametric threshold) in the optical domain. While in the electrical domain, noise from the measurement system is much higher than the piezoelectrically transduced thermomechanical noise. Once the device is parametrically pumped, electrically transduced thermomechanical noise is greatly amplified and gradually appears above the electronic noise level near the parametric pumping threshold. Above this level, we have achieved noise matching. Based on the comparison between the parametric pumping in the optical and electrical domain, we find that although the piezoelectrically transduced thermomechanical noise is ~46 dB below the noise level of the typical electronic measurement system, the parametric pumping can greatly amplify the signal to emerge above the electronic noise level, allowing us to electrically detect the thermomechanical resonance and enhance SNR, suggesting the possibilities of improving performance of NEMS/MEMS devices for building sensors and oscillators.

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MN-Contributed On Demand-7 $MoTe_2$ NEMS Resonator for Near-Infrared Light Detection*, S M Enamul Hoque Yousuf,* *X. Zheng, P. Feng,* University of Florida, Gainesville

In recent years, molybdenum ditelluride ($MoTe_2$) has received significant attention [1] due to its unique semiconducting and phase transition properties [2]. Semiconducting 2H-$MoTe_2$ is known to have thickness-dependent bandgap from 0.83 eV (bulk) to 1.1 eV (monolayer) where bandgap also changes from indirect to direct. Ultrasensitive near-infrared (NIR) light detection is desirable in NIR imaging, surveillance, communication, and security applications. High-end commercial NIR detectors require cryogenic cooling to reduce the thermal noise, which limits their applications in broader fields. As an alternative solution, transducers enabled by nanomechanical resonators have been proposed [3]. The bandgap of monolayer 2H-$MoTe_2$, which matches that of silicon (1.1 eV), is narrower than the bandgaps of other transition metal dichalcogenides and makes it a suitable candidate for visible and NIR light detection.

In this work, we fabricate $MoTe_2$ drumhead resonators on sapphire substrate with local electrostatic gates. After forming Au/Ti top electrodes, we transfer a $MoTe_2$ flake with desired shape and thickness on to the predefined sapphire substrate using all-dry transfer method through a custom-built transfer stage. Since the tellurides are more prone to ambient degradation than selenides or sulfides, the $MoTe_2$ flake is encapsulated by hexagonal boron nitride (h-BN) thin layer and is stored in vacuum all the time. To confirm the identity of the constituent crystal of the resonator, we use Raman spectroscopy with a laser at λ = 532 nm. The measured data clearly shows characteristics of Raman modes confirming the high quality of the suspended 2D $MoTe_2$ crystal. We then measure the transistor properties of the fabricated device. The transfer curve shows a p-type behavior with $I_{On}/I_{Off} > 10^4$; and the transport curve shows an ohmic contact between the $MoTe_2$ and the Au electrodes. We measure the resonance of the device by using an optical interferometry system [4] and obtain a fundamental-mode resonance at 12.24 MHz. We further measure the NIR response of the drumhead resonator by illuminating the device using a 785 nm laser. This study provides an initial exploration in building $MoTe_2$ NIR detectors.

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MN-Contributed On Demand-10 Interposer Fabrication with Heterogeneous Integration of Multi-Project Wafer Die for Mid-Volume RF Microsystems

Mieko Hirabayashi*, S. Lepkowski, S. Herrera, C. Nordquist, C. Gibson, A. Ruyack, J. McDow, A. Hollowell, M. Jordan,* Sandia National Labs

We demonstrate a radio frequency (RF) interposer with built in passive components and the ability to accept 2.5D heterogeneously integrated die. 2.5D heterogenous microsystems allow for the use of modular, commercial off the shelf or multi-project wafer components and/or disparate technologies like Si and GaN based semiconductors. The RF interposer is formed using glass wafers to prevent substrate coupling. The passive components are produced utilizing patterned copper electroplating followed by a spin-on interlayer dielectric.

High density flip-chip interconnects can be cost prohibitive during prototyping and for low volume applications. For example, if a multi-project wafer component is used, the die are delivered singulated and often with Al as the top metal, which by itself is not compatible with flip-chip interconnects. This then leads to labor intensive patterning and under bump metallization processes at the die level. We demonstrate a lithography-free, batch level under bump metallization process utilizing electroless plating to form ENEPIG terminated connections. We are able to show that the process is compatible with gold pillar and SnAg capped Cu pillar interconnects.

Gold interconnects are of interest for this application because of their high ductility and compatibility with III-nitride semiconductors. However, the mechanisms of gold-gold bonding are not well studied in microelectronics. Gold-to gold bonding and gold-to-sputtered gold nickel studs have been demonstrated, however the lack of a suitable model for gold-to-ENEPIG bonding led us to investigate the process more closely. This led us to interesting conclusions regarding the relationship between the bonding force, aspect ratio, and overall deformation of the gold pillars required to achieve acceptable bonds.

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MN-Contributed On Demand-13 Scaling Copper Deposition in Through-silicon Vias from Die Level to Wafer Level Plating

Jessica McDow*, R. Schmitt, M. Hirabayashi, E. Baca, J. McClain, L. Menk, A. Hollowell, M. Jordan,* Sandia National Laboratories

Copper-filled through-silicon vias (TSVs) are a key technology for 3D integration of microelectronic devices. 3D integration enables system miniaturization, increases bandwidth per volume, and improves device performance. Full wafer thickness vias are utilized for microelectromechanical systems (MEMS) devices where additional mass of the full wafer is advantageous. For high-power devices, large scale vias or via arrays can be used both to supply power and for thermal management. Utilizing the s-shaped negative differential resistance (S-NDR) mechanism[2], Cu deposition for full wafer thickness TSV geometries in a suppressor-based electrolyte consisting of copper sulfate, sulfuric acid, potassium chloride, and Tetronic 701 suppressor has been achieved.[1] Typically, void-free bottom-up filling with these additive-based electrolytes is performed through potentiostatic deposition with a reference electrode. However, to transition this process to a production scale wafer plating tool, a current-controlled plating regime is required because these tools are not equipped with reference electrodes. Voltage-controlled electrochemical deposition (ECD) parameters have been developed through the S-NDR mechanism for bottom up filling of vias, where potential stepping was performed from -500 mV (MSE) to -560 mV (MSE) in -10 mV increments, and each potential was held for 2 to 5 hours to ensure a void-free fill.[1] This process was used in die level scaling experiments to derive a current-controlled ECD procedure and understand the relationship between applied current density, total conductive surface area, and active via area.

Various applications for TSVs and downstream processes can occur at elevated temperatures. Understanding deformation and stress of Cu-filled TSVs that occurs during thermal cycling is important to the TSV reliability. Experiments were performed to characterize the protrusion of 30 um diameter - 100 um depth Cu-filled TSVs, where an optimized annealing profile was proposed to suppress grain growth during thermal cycling.[3] Annealing studies are currently being conducted on full wafer thickness Cu-filled TSVs to determine an optimal temperature cycling profile for the protrusion behavior of mesoscale TSVs. This work presents the results of a current-controlled wafer level Cu deposition process and thermal characterization of high aspect ratio mesoscale TSVs.

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MN-Contributed On Demand-16 Device Fabrication Process for Controlled RF Plasma Breakdown

Sergio Herrera*, A. Ruyack, M. Jordan, C. Moore, G. Hummel, M. Ballance, A. Bingham, A. Schiess, C. Gibson, C. Nordquist,* Sandia National Labs

Paschen's curve expresses the required voltage to create electric arcing between two electrodes (breakdown voltage) as a function of gas pressure, temperature, and the gap between them. At atmospheric pressure the Paschen relation fails at small (<5µm) gap distances due to small numbers of gas molecules between the electrodes (pseudo-vacuum condition) and the advent of electron tunneling phenomena which is enhanced by ions near the cathode.Extensive research has been conducted to characterize voltage breakdown behavior of large gaps, however little has been done to understand the high frequency breakdown of narrow gaps. In the world of microsystems, the gap size is approximately equal to the ionization mean free path of electrons (at atmospheric pressure), allowing for field emission, ion-enhanced field emission, and other mechanisms to exercise greater dominance.

Here we present on the breakdown characteristics of wafer fabricated vertical and horizontal micron-scale radiofrequency (RF) plasma discharge devices. Device breakdown gaps vary from 100 nm to several microns. Precision electroplating of high-stiffness gold combined with wet release of gold microbridges is used to produce discharge gaps for vertical devices. Dual sacrificial layers (allowing for more controlled spacing) and dry MEMS release techniques are incorporated to locally maximize the electric field.At these low discharge gaps, we expect to promote deviation from classical Paschen curve behavior with the potential for sub 10 V breakdown. Improved understanding of these relations will enable approaches for both mitigating high-frequency breakdown and the prospect for new classes of devices.

This work is supported by the Laboratory Directed Research and Development program at Sandia National Laboratories, 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-NA-0003525. This paper describes objective technical results and analysis. Any subjective views or opinions that might be expressed in the paper do not necessarily represent the views of the U.S. Department of Energy or the United States Government.

MN-Contributed On Demand-19 Resonant Motion and Frequency Tuning in Nano-Electromechanical Devices Based on Two-Dimensional Semiconductor WSe_2

Yachun Liang*, J. Zhu, F. Xiao, S. Wu, C. Jiao, Z. Wang,* University of Electronic Science and Technology of China

Introduction

Two-dimensional (2D) materials, like graphene and transition metal-dichalcogenides (TMDCs), have been extensively explored because of their intriguing physical properties. Nanoelectromechanical system (NEMS) resonators based on 2D materials hold great promises for transducers and signal processing devices [1,2]. Atomically-thin WSe_2 has demonstrated good potential towards high quality-factor NEMS resonators [3]. Here, we demonstrate WSe_2 resonators with tunable frequency at room temperature.

Methods

In this work, WSe_2 resonators are fabricated using an all-dry transfer method with pre-patterned substrate, and the fabrication progress is shown in Fig. 1 [4]. We investigate the frequency tuning in WSe_2 resonators, by using a custom-built 2D NEMS resonator measurement system, including laser interferometry readout, optical excitation (Fig. 2); electrical driving (Fig. 3); and the capability of measuring thermomechanical motion without external driving (Fig. 4).

Results

We first explore the optical driving and optical readout measurement, where we connect the output of the Network Analyzer to the input of a 405 nm modulated laser (driving), which is aligned to share the same optical path with the 633 nm detection laser(Fig. 2a). Specifically, the output the RF signal controls the 405 nm laser power, which periodically drives the WSe_2 resonator through optothermal effect. The device shows a clear response frequency in MHz range (Fig.2b), and the resonance frequency increase with the magnitude of the DC gate voltage V_g^{DC} (Fig. 2c).

We further investigate the gate tuning using electrical driving (Fig. 3a). The output of RF signal periodically drives the WSe_2 membrane, and resonance response detected by 633 nm laser can be observed when V_g^{DC} is 2 V (Fig. 3b). In this case, clear frequency tuning is also observed (Fig. 3c). We measure the thermomechanical resonant response with 633 nm laser detection as is shown in Fig. 4a. It shows a pronounced resonance peak in the noise spectrum, consistent with the optical and electrical driving schemes. The measured thermomechanical frequency can be tuned by V_g^{DC}.

Summary

We have explored frequency tuning in WSe_2 NEMS resonators for optically driving resonances, electrically driven resonances, and completely un-driven thermomechanical resonances, all under room temperature. Our results suggest that WSe_2 NEMS resonators can be explored for future frequency-tunable NEMS devices operating at room temperature.

Reference

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MN-Contributed On Demand-22 Observation of Temperature Coefficient of Frequency (TC*f*) Reversalin Bismuth Oxyiodide (BiOI) Vibrating Nanomechanical Resonators*, Fei Xiao, S. Wu, J. Zhu, Y. Liang, C. Jiao, S. Pei, Z. Wang,* University of Electronic Science and Technology of China

Introduction

Atomically thin two-dimensional (2D) materials, like graphene and transition metal-dichalcogenides (TMDCs), have attracted tremendous attention because of their intriguing material properties. Nanomechanical resonators based on 2D materials have been investigated, demonstrating great potential towards applications such as transducers and signal processing devices[1,2]. Bismuth oxyiodide (BiOI) is an emerging three-element 2D layered material[3]. Here, we report experiment demonstration of the first BiOI resonators, and its unusual temperature coefficient of frequency (TC*f*).

Methods

In this work, BiOI nanomechanical resonators are fabricated using a typical dry-transfer method[4], with BiOI flake connected to the electrode patterned by evaporation. We characterize the resonant response using a scheme that incorporates electrical driving and optical detection (Fig. 1a). Vibrations in the BiOI resonator are electrostatically excited though the back gate and interferometrically detected with a 633 nm laser focused on the suspended flake. For all measurements, the resonator sample is mounted in a temperature-controlled sample stage under high vacuum (10^{-4} mbar).

Results

We first characterize the thermomechanical resonance without external drive (Fig. 1b), and a clear resonance peak is observed in the noise spectrum, with the resonance frequency f_{res} = 3.86 MHz. We further explore driven response in BiOI resonators using electrical excitations with V_g^{DC} = 1 V, and investigate the TC*f* in these devices.

At first (294-302K), frequency f_{res} rapidly decreases as temperature increase. However, when the temperature is increased above 302 K, f_{res} rapidly increases with temperature (Fig. 2). By using the room temperature (294 K) data as reference (Fig. 3b), we calculate a TC*f* of -0.365%/K for the device below 302 K, and +0.412%/K above 302 K. Fig. 3a and 3c show the measured resonances of a BiOI resonator and optical images at 294 K and 324 K, respectively. We will present more details about the observed TC*f* inversion and its physical origin in the full presentation.

Summary

We have studied TC*f* in BiOI nanomechanical resonators, for electrically driven resonances with temperature from 294 to 324 K. This device shows very high TC*f* values, and a TC*f* inversion is observed around 302 K.Our results suggest that BiOI nanomechanical resonators can be explored for temperature sensitive resonant sensors.

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MN-Contributed On Demand-25 Gate-Switchable Bistable Nanomechanical Resonators Based on Two-dimensional Molybdenum Sulfide*, Chenyin Jiao, B. Xu, J. Zhu, F. Xiao, Y. Liang, J. Chen, S. Pei, J. Xia, Z. Wang,* University of Electronic Science and Technology of China

Introduction

Nanomechanical resonators based on 2D materials have been widely investigated, demonstrating great potential in applications such as sensors and signal processing devices[1]. While typically the frequency can be continuously tuned by applying a gate voltage, it is challenging to realize a resonator that can switch between two distinct states, both of which can be maintained without any external voltage[2][3].

Here we demonstrate a bistable nanomechanical resonator based on two-dimensional molybdenum sulfide (MoS_2), which has two stable resonant states that can be switched using gate voltage. We use electrostatic force to laterally pull a nearby structure in order to switch the tension in the 2D resonator, and the frequency change can be maintained without any external voltage.

Methods

The MoS_2 nanomechanical resonator is fabricated by mechanically exfoliating MoS_2 crystal onto Si/SiO_2 substrates with pre-patterned cavities and electrodes[4]. We measure the resonant response using a customized scheme that incorporates electrical driving and optical detection (Fig. 1). We also characterize the tension in both the suspended part and on-substrate part of the MoS_2 flake to monitor its tension before and after gate switching (Fig. 2).

Vibrations in the MoS_2 resonator is electrostatically excited through the back gate and interferometrically detected with a 633 nm laser focused on the suspended flake. For all measurements, the resonator sample is mounted in a sample stage under high vacuum (10^{-3} mbar).

Results

We first measure the resonant response of the device with 0 gate voltage, and find its resonance frequency f_{res}= 6.33 MHz. We then gradually increase the gate voltage from 0 to 29 V (Fig. 3a), and then back from 29 V to 0 V (Fig. 3b). It can be clearly seen that the evolution of resonant frequency with gate voltage does not follow the previous trajectory, and upon returning to 0 gate voltage the f_{res} has increased from 6.33 MHz to 7.65 MHz, clearly illustrating the two distinct resonant states.

We further show that the 0 gate voltage resonance frequency can be switched back and forth through gate voltage sweeps, and that the bi-stability is due to the lateral tensioning through interaction with a nearby larger membrane, which we will present with additional details at the symposium.

Summary

We have demonstrated gate-switchable MoS_2 nanomechanical resonators with two distinct and stable resonant states, which can be controlled by gate-induced tension in the structure. Our results show that such devices hold promises for reconfigurable resonators that can be easily switched using voltage.

Reference

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MN-Contributed On Demand-28 Thermally Released Spring-Loaded Platform for Capsule Based Drug Delivery and Sensing, ***Joshua Levy****, J. Stine, L. Beardslee, R. Ghodssi,* University of Maryland, College Park

The human gastrointestinal tract (GIT) has emerged in recent years as a medium for probing integral biological phenomena within the body, elucidating many underlying mechanisms of chronic diseases. To better understand these interactions, targeted treatment and monitoring within the GIT has been performed using endoscopic probes and capsule-based platforms. There is much research available demonstrating actuation mechanisms for targeted drug delivery and sensing applications utilizing an embedded balloon or spring to insert a microneedle type structure into the subepithelial space. These devices frequently rely on pH changes in the intestinal tract to trigger actuation, lacking control and limiting the system to passively triggered actuation. Therefore, the development of release mechanisms that can be triggered rapidly and on-demand would enable more precise and targeted therapeutic delivery and sensing.

Here we report the design and fabrication of a novel thermally released 3D-printed spring (Fig. S1) and microfabricated heater as a platform for drug delivery and sensing within epithelial tissue. The spring (H=8 mm and D=3 mm) was fabricated with a high resolution (30 µm) Digital Light Processing 3D printer using a 40:60 mixture of high- and low-modulus Monocure resin to achieve the desired spring flexibility and strength. To fix the spring in a compressed state a low-melting point (60 C) polymer, polycaprolactone, was applied to the base of the spring and bonded to a 4 mm pillar extending down from the spring tip. The 3 mm diameter resistive microheater was comprised of a Cr/Au (20nm/100 nm) coil patterned on a flexible polyimide substrate through a laser cut mask using electron beam evaporation. The heater design maintains a resistance of 50 Ohm, such that the current through the resistor is compliant with the maximum allowable current from a 3-V 2L76 coin cell battery (60 mA).

The mechanical properties of the spring were characterized using a mechanical tester, observing a spring constant of 13.6 mN/mm (Fig. S2). This force constant is sufficient to insert a microneedle-based drug delivery or sensing system into the epithelial gut layer, as we have previously demonstrated a microneedle tissue insertion force of 0.6 mN. To express the triggered release of the compressed spring, a current of 60 mA was applied to the microheater and successful release of the spring mechanism was achieved within 30 s. Further integration of the spring-heater platform into an ingestible capsule provides potential for targeted drug delivery and sensing within the GIT.

MN-Contributed On Demand-31 Sidewall Nanochannel Fabrication Using Membrane Projection Lithography and Metal Assisted Chemical Etching, ***Tong Dang****,* University of Pennsylvania*; R. Chaudhary,* ETH Zurich, Switzerland*; N. Xie,* University of Washington*; G. Kim, G. Watson,* University of Pennsylvania

Horizontally enclosed nanochannels have a wide variety of microfluidic applications ranging from biochemical sensing to electrochemical energy conversion and transport [1]. While top-down fabrication of horizontal nanochannels has been reported in materials such as silicon dioxide and polymers, less research has been focused on silicon based horizontal nanochannels. In this work, we report an approach consisting of membrane projection lithography (MPL) [2] and metal assisted chemical etching (MacEtch) [3] to fabricate nanochannels with tunable sizes and shapes that run parallel and beneath the surface of an Si substrate [4]. 2 µm deep Si trenches are first patterned using a direct laser writer and etched using deep reactive ion etching (DRIE) to form smooth sidewalls. Au disks are then deposited onto the sidewalls using MPL, where Au is evaporated at a 45 degree angle through an electron beam lithography (EBL) patterned surface membrane. The Au disks then serve as a catalyst in the MacEtch process to form the nanochannels, in which the silicon directly underneath the Au disks is removed. The fabricated nanochannels are characterized using scanning electron microscopy (SEM), providing insights into effectiveness of the fabrication approach.

This work focuses specifically on the following aspects for enhanced reliability and reproducibility of the approach: improving the smoothness of the DRIE fabricated sidewalls; optimizing the planarization process preceding the patterning of the MPL layer; characterizing the lithography-created trenches and patterns to avoid any pattern size bias leading to misalignment and identifying the direction of the Au disk movement through the Si sidewall.

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MN-Contributed On Demand-34 On-Demand Reconfigurable Transmission Grating for Neutron and X-ray Interferometry, ***Sarah M. Robinson****,* National Institute of Standards and Technology (NIST)/ University of Maryland, College Park*; R. Murphy, K. Weigandt, D. Hussey, N. Klimov,* National Institute of Standards and Technology (NIST)

We report on the development of a real-time reconfigurable transmission grating for neutron and x-ray interferometry. Such dynamic grating can be used as source of a quasi-coherence for phase imaging using incoherent sources of radiation such as neutron or x-ray beams. Our DynAmic ReconfIgUrable Source grating (DARIUS) is a silicon-based microfluidic device, which allows on-demand modulation of neutron and/or x-ray intensity in one dimension by adjustment of transmission grating period ranging from 20 µm to 20,000 µm. The main component of the DARIUS device is 51.2 × 51.2 mm^2 transmission grating consisted of 2,560 microfluidic diffraction channels etched in silicon with 10 µm x 100 µm (width × depth) cross-section and 20 µm pitch. Transmission grating period tunability is realized by dynamically changing the channels' opacity to neutrons and/or x-rays. Opacity of each of 2,560 diffraction channels can be switched independently between non-transparent and transparent state by filling/draining the channels with neutrons/x-ray absorbing fluid. In this work, we will provide details on the fabricating the first prototype device, DARIUS-1, consisting of 128 independently controlled channels. We will also discuss our method of channel's infilling with opaque fluid and overall device performance.

MN-Contributed On Demand-37 QCM Study of Tribotronic Control in Ionic Liquids and Nanoparticle Suspensions, ***Caitlin Seed****, B. Acharya, J. Krim,* North Carolina State University

A Quartz Crystal Microbalance (QCM) technique has been employed to tune friction at liquid-solid interfaces with tribotronic methods employing externally applied electric fields in both nanoparticle suspensions and ionic liquid systems. The setup consists of a QCM immersed in liquid containing electrically charged constituents whose sensing electrode faces a nearby counter electrode. An electric field perpendicular to the QCM surface is created when a potential is applied between the two electrodes, which allows the charged constituents in the surrounding liquid to be repositioned. QCM measurements are able to detect differences in friction under various field conditions, and thus detectably tune the friction in both nanoparticle and ionic liquid systems. The versatility and simplicity of QCM friction measurements renders it an ideal tool for the rapidly expanding research area of tribotronics.

MEMS and NEMS Group
Room On Demand - Session MN-Invited On Demand
MEMS and NEMS Invited On Demand Session

MN-Invited On Demand-1 Printed and Biodegradable Sensors for Real-Time High-Spatial Density Monitoring of Soil Conditions*, Gregory Whiting, Y. Sui, M. Atreya, G. Marinick, J. Nielson, A. Gopalakrishnan,* University of Colorado Boulder*; R. Khosla, S. Dahal, W. Yilma,* Colorado State University*; A. Arias, C. Baumbauer, M. Payne, D. Wong, P. Goodrich,* University of California Berkeley **INVITED**

An understanding of soil properties are of critical importance for optimizing agricultural input use (such as irrigation water and fertilizer) and for general land management strategies. However, obtaining information about soil properties in real-time can be a challenge, which limits management approaches, and can lead to excess input and energy use, reduced profitability, and environmental concerns. Remote imaging can provide high-resolution, but measurements may be infrequent, impacted by weather and plant growth, and could requires inference to determine properties of interest. Installed sensors that directly sample soil can directly provide the desired information directly, but are often bulky and expensive, limiting their use to a small number of sensors per field. This is a concern since many important species of interest (such as soil nitrate), can vary significantly (on the order of 10s of meters), as such, ideally, higher spatial density measurements are needed to capture current conditions and enable optimized management strategies.

In this presentation a number of devices (capacitive, ion-selective, and enzyme/microbe selective) recently developed for real-time, in-situ, high-spatial density monitoring of soil conditions such as moisture and ion (particularly nitrate) concentration, and microbial activity will be discussed. In order to enable broad distribution of large numbers of devices over large areas, these sensors are fabricated using additive printing techniques (such as screen printing) and biodegradable materials for substrates, conductors, encapsulants, stimuli-responsive materials, etc.), so that the sensors degrade harmlessly into the soil when no longer required, enabling large amounts to be used without the need for maintenance or collection or the production of excess waste.

MN-Invited On Demand-7 Chip-scale Atomic Devices*, John Kitching,* NIST **INVITED**

Since the invention of the chip-scale atomic clock in 2001, and its subsequent commercialization in 2011, many research groups and companies worldwide have begun programs to develop similar or related instruments. In this talk, I will present recent work in the Atomic Devices and Instrumentation Group at NIST to develop next-generation devices based on silicon micromachining, atomic spectroscopy and photonics. This will include photonically integrated atomic wavelength references, chip-scale optical clocks and novel atomic diffractive optical elements. I will conclude with a discussion of “NIST on a Chip”, a new effort at NIST to provide low-cost SI calibration at the chip-scale across a range of physical quantities.

MN-Invited On Demand-13 Towards Eliminating Friction and Wear in Micro-Machines to Macroscale Mechanical Systems*, Anirudha Sumant,* Argonne National Laboratory **INVITED**

Every moving mechanical system consisting of contacting/sliding/rotating contacts ranging from nanoscale switches, micro-machines to large macroscale systems such as wind turbines suffers from the energy loss due to wear and friction and it amounts to roughly a quarter of total energy loss worldwide. There is growing demand to develop advanced coatings and lubricants that can not only reduce the energy loss but also last longer, can work in any environment, don’t need replenishment, cheaper to produce on large scale and most importantly are environment friendly. In this context, I’ll discuss our research efforts, which are focused on understanding the atomic scale origin of the friction and how nanoscale interactions of materials at the sliding interface could be manipulated to have its impact on the macroscale. I’ll review our earlier work on demonstrating diamond-based micro-machines with almost no wear even after millions of cycles of operations as it forms impervious tribolayer after initial run-in and some recent work on utilizing a combination of 2D materials and nanoparticles as a solid lubricant in reducing friction and wear to near zero (superlubricity) in rough steel contacts at macroscale. I’ll discuss the underlying mechanism in both cases and how one can translate these fundamental discoveries into real-world applications by working collaboratively with industry.

MN-Invited On Demand-19 Visualization of Nanoscale Contact by in situ AFM-TEM Experiments: Sliding-Dependent Adhesion of Si, and Wear at the Interface MoS2-MoS2 Interface*, Robert Carpick,* University of Pennsylvania **INVITED**

I will discuss nanoscale asperity-on-asperity contact and sliding experiments conducted using an *in situ* nanoindentation apparatus inside a transmission electron microscope (TEM). The instrument has been customized to permit atomic-scale resolution of contact formation, asperity sliding, and adhesive separation of a nanocontact with real-time TEM imaging [1-7], with a new innovation in the instrumentation that allows two AFM tips to be studied in dynamic loaded contact [6, 8]. Forming and separating the contacts without sliding revealed small adhesion forces; sliding during retraction resulted in a nearly 20 times increase in adhesion. These effects were repeatable multiple times. We attribute this surprising sliding-dependent adhesion to the removal of passivating terminal species from the surfaces, followed by re-adsorption of these species after separating the surfaces [8]. Preliminary results from molecular dynamics simulations to elucidate this effect will be discussed. I will also present new results from nanocontact experiments of 2D materials obtained *in situ* using transmission electron microscopy (TEM). We have observed tip-on-tip contact and sliding behavior at the nanoscale for self-mated contacts of few-layer MoS_2, revealing intrinsic contact, adhesion, and friction properties of these ultrathin layers. I will present results comparing the behavior of nanometer-scale thick MoS_2 layers with different degrees of nanocrystallinity, and discuss collaborative work modeling these experiments using molecular dynamics simulations.

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Manufacturing Science and Technology Group
Room On Demand - Session MS-Contributed On Demand
Manufacturing Science and Technology Contributed On Demand Session

MS-Contributed On Demand-1 Machine Learning and Simulation Assistant Technology to Facilitate 3d Memory Analysis of Cross Section Sem Images*, M. Bryan, J. Foucher, Julien Baderot,* POLLEN Metrology, France

We present a method for fast, enhanced cross-section SEM metrology of 3D memory channels through simulation and machine learning. Using simple geometric models of the channel structure and certain assumptions on the behaviour of the electron beam we demonstrate that our method provides increased robustness to acquisition errors and gives more physically meaningful measurements of 3D memory when compared to traditional image processing-based techniques. We show also how this technique can be integrated into the Process Engineer workflow during semiconductor research and development, providing actionable results faster and reducing overall time-to-production

MS-Contributed On Demand-4 Atomic-Precision Position Error Correction for Dopant-Array Quantum Devices*, James H.G. Owen*, *E. Fuchs, M. Haq, J. Randall,* Zyvex Labs

For dopant-based atomic-scale devices such as the 'single atom transistor' [1] and 2D Quantum Metamaterials[2], arrays of dopant patches need to be fabricated with atomic precision for both the size of the patches (to control the number of dopants in each patch) and the relative positioning of the patches in the array (to control the interactions between patches). As the number of patches scales up from a 3x3 array to a 32 x 32 array, this requires an automated writing process, without losing atomic precision patterning.

Various types of positioning errors are evident in the arrays. 'Staircasing' is the gradual upward drift of the boxes along each row, in alternating directions. 'Phase shift' is the misalignment of the boxes from one row to the next, which can reach a 180° phase shift. 'Curvature' or 'shearing' are distortions of the overall array shape. Various different sources of tip position error cause these distortions, including lattice lock misalignment, piezo creep and hysteresis, and thermal drift.

We are working to remove as many of these sources of imprecision as is possible, so as to achieve atomic precision dopant arrays of arbitrary size. Performing simulations of array fabrication which include deliberate errors of one type or another helps to isolate the source of the observed distortions, so that they can be corrected. 'Staircasing' is the result of drift, which can also affect the lattice lock, and therefore cause misalignment of the patterning with the lattice. 'Phase shift', however is indicative of xy creep. Shear and Curvature can be caused by uncorrected slow creep, or by variation in the rate of drift caused by temperature fluctuations in the lab.

By comparing the simulations with experimental data, we can determine which parameter, i.e. creep, hysteresis or drift correction, needs to be adjusted. We show that after adjustment we are able to draw arrays where the positioning errors are no more than 1 px.

Even with perfect positioning, the patches may not be the correct size due to sub-px position errors, stochastic errors such as tip changes, and incomplete lithography. We are working on machine-learning-based image recognition techniques to identify these defects, and correct them in an automated process.

In this way, we hope to be able to draw large arrays while maintaining atomic precision, which will enable Analog Quantum Simulations, and eventually 2D Quantum Metamaterials.

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Manufacturing Science and Technology Group
Room On Demand - Session MS-Invited On Demand

Manufacturing Science and Technology Invited On Demand Session

MS-Invited On Demand-1 Control of Plasma and Surface Reactions for Atomically Precise Device Fabrication*, Tetsuya Tatsumi,* Sony Semiconductor Solutions Corporation, Japan **INVITED**

According to the IRDS,[1] along with the progress of miniaturization in the future, technologies to control the processing at the atomic level to respond to new materials and new structures, including 3D stacked devices and new devices called Beyond CMOS, will be required. However, plasma and surface reactions are still often treated as black boxes in dry etching process control, and quantitative understanding and control of plasma processes will be more important for achieving high-precision processing. This paper briefly outlines the development history of dielectric film dry etching equipment and processes used to achieve high-precision processing characteristics and describes what is required for processing at the atomic layer level. In the 1980s and 90s, the development of a plasma sources with a high ion flux to increase the processing speed of SiO_2, and a process that strictly controlled the number of electron collisions ($\tau n_e\langle\sigma v\rangle$) to suppress excessive dissociation of gas molecules to achieve high selectivity was established.[2] With the advent of low-k materials to realize high-speed, low-power devices, around 2000, a model for more delicate control of surface reactions and techniques for predicting incident flux have been proposed.[3] From 2010 onwards, techniques for predicting damage that cannot be observed with an electron microscope have been required.[4-5] Therefore, the energy distribution of incident ions and the penetration depth of high-energy particles have been quantitatively controlled. More recently, there have been active discussions about SiO_2 ALE.[6] In this process, however, since the reaction does not stop by self-limiting, it is necessary to predict and control the surface state when using plasma in the transient state before reaching the steady state.[7] In addition, latent defects[8] that cannot be recovered by heat treatment must be managed. We believe that technologies such as plasma monitoring, modeling, and prediction technologies will be further improved, and future atomic-level manufacturing technologies will be realized.

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MS-Invited On Demand-13 Ion Tunable Electronic Materials Systems for Neuromorphic Computing*, Alec Talin,* Sandia National Laboratories **INVITED**

Tuning electronic conductance through solid state electrochemical ion insertion has emerged as a promising technology to enable next-generation, ultralow energy computing architectures$^{1-3}$. Unlike two-terminal non-volatile memory elements, the three-terminal redox transistor decouples the 'write' and 'read' operations using a 'gate' electrode to tune the conductance state through charge transfer reactions involving ion injection into the channel electrode through a solid-state electrolyte. The insertion of ions into the bulk of the channel acts to dope the material through a gradual composition modulation that leads up to thousands of finely spaced conductance levels (synaptic weights) with near-ideal analog behavior. These properties enable low-energy operation without compromising analog performance and non-volatility. However, the strong coupling of ionic and electronic processes sharply challenges our current understanding of solid-state electrochemical systems, particularly at decreasing dimensions and timescales relevant to computing technology. In my talk I will discuss the rich portfolio of challenging, exciting fundamental science questions about ion tunable electronic materials systems and how we can harness these to realize a new paradigm for low power neuromorphic computing.

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3. Li, Y. Y.;Fuller, E. J.;Asapu, S.;Agarwal, S.;Kurita, T.;Yang, J. J.; Talin, A. A., Low-Voltage, CMOS-Free Synaptic Memory Based on Li_xTiO_2 Redox Transistors. *Acs Applied Materials & Interfaces* **2019,***11* , 38982.

MS-Invited On Demand-19 Digital Electronics at the Atomic Scale*, Shashank Misra,* Sandia National Laboratories, USA **INVITED**

Tooling and development costs are poised to disrupt the microelectronics ecosystem, as they dramatically increase the risk in choosing a path to further shrink transistors from the nanoscale to the atomic scale. In this context, relaxing the requirement for achieving scalable manufacturing allows us to evaluate opportunities based on the physical limit of atoms, and not just based on incremental gains. Here, we examine progress in creating digital microelectronics using atomic precision advanced manufacturing (APAM), which uses a scanning tunneling microscope to pattern atomic resists at the surface of silicon with atomic precision, templating dopant precursor incorporation at the surface of silicon. By analogy, APAM functions as a pathway to area-selective doping.

For microelectronics, the value proposition for APAM devices is not in making single atom transistors that function at cryogenic temperatures. Rather, it derives from the ability to create atomically abrupt doping profiles whose density far exceeds the solid solubility limit, dramatically altering the electronic structure of silicon, and with more modest thermal budget requirements than ion implantation. These qualities motivate our re-evaluation of the vertical tunnel field effect transistor (TFET), whose long-promised energy efficiency compared to field effect transistors has been hindered by abruptness with which doping profiles can be defined. Despite this promise, APAM has mostly been used to fabricate simple "one-off" devices that function only at cryogenic temperatures. The first part of this talk will focus on our progress towards fabricating the first APAM-based TFET, including operating devices at room temperature and with a modern gate stack. The second part focuses on our work in establishing proofs-of-principle for manufacturability, including our efforts to directly integrate APAM into a CMOS manufacturing workflow and to extend APAM to volume wafer-scale fabrication at reduced lateral resolution. Along with the vertical TFET, the near-term application of reducing contact resistance in modern transistors only requires atomic precision in epitaxy as opposed to atomic precision laterally.

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MS-Invited On Demand-25 Extending Semiconductor Patterning Into the Next Decade*, Michael Lercel,* ASML **INVITED**

Scaling has enabled the semiconductor industry to be vibrant and growing for decades. Current market drivers continue to show a current and future strong demand for semiconductors. So the long term industry outlook is good – can technology keep up? Advanced patterning is dependent on having the right lithography, process, and metrology tools. Printing small features is not enough – tight control of tolerances, good yield, and cycle time are essential for manufacturability.

EUV is now positioned to enhance logic and memory processes with improved cycle time, less variability from multiple processes, and reduced process complexity compared to multiple patterning. Production with EUV is underway, so now the question becomes how does EUV enable the 3nm node and beyond.

EUV layer adoption is anticipated to increase at 5nm logic node versus the 7nm logic node where it is being first introduced. The same benefits of reduced process complexity, shorter cycle time, and reduced variability are now expanded as an all-optical 5nm logic node would involve nearly 100 mask levels. Beyond the 5nm logic node, higher Numerical Aperture (NA) EUV will further extend EUV single exposure resolution to enable Moore's law scaling to the 3nm node and beyond.

In this presentation, we review the progress on enabling EUV for logic and memory manufacturing with progress on productivity, overlay performance, and availability of the EUV scanner plus the metrology and infrastructure progress to enable high-volume manufacturing. The extensions to enable EUV for 5nm node logic, and the preparation of high-NA EUV for 3nm and beyond node logic will be reviewed.

Nanoscale Science and Technology Plenary Session
Room On Demand - Session NP-Invited On Demand

Nanoscale Science and Technology Plenary Invited On Demand Session

NP-Invited On Demand-1 Atom-Defined Silicon Circuit Elements For Fast, Low Power Computing*, Robert Wolkow,* University of Alberta and The National Institute for Nanotechnology, Canada **INVITED**

CMOS based computers cannot be made substantially more energy efficient or faster. Fast, low power field controlled computing schemes believed capable of reviving Moore's law have not been physically realizable, until now. In such an approach binary information is encoded in spatial charge arrangements among quantum dots. Available quantum dots had been too large, too irregular, and too prone to debilitating charge trap effects. By reducing the quantum dot to a single silicon atom we have made the single electron charging energy very large resulting in dramatically improved noise immunity while also gaining near perfect homogeneity of components and eliminating charge traps. These structures are absolutely stable to over 200 C. And crucially, the silicon atom printing process has been automated and rendered virtually error free.

We will discuss how the atom-scale circuitry works and why it consumes little power ("Binary Atomic Silicon Logic", Nature Electronics, 1, 636-643). Atom defined binary wires will be shown. These transmit information extremely rapidly and without the use of conventional current and as a result experience virtually no I^2R heating. We will also show a working binary logic gate.

The A.I. automated fabrication process and atomic editing will be explained. Also the merging of regular CMOS with atom scale circuitry will be shown. This hybrid CMOS/Atom approach minimizes time to deployment. We can use CMOS circuitry where it is adequate and deploy the atom circuitry as embedded enhancements to reduce power, increase speed, or achieve all-new functions. Three applications will exemplify the advantages of this approach.

85. A neural network simulator will be described that has the potential to deliver Gibbs samples, obviating MCMC sampling when performing unsupervised training on unlabeled data (Phys. Rev. Lett., 121, 166801).
86. The low power prospects of our circuitry are shown by simulating the Google TPU with an atom-defined MXU. Clocking power is reduced 10,000x at 1 GHz. Alternatively, by allowing today's power consumption (limited to 100 W/cm2 dissipation) clocking of 1 THz becomes achievable.
87. The MXU is for now out of reach because it requires millions of atom printing steps. A practical, ~thousand atom goal is an extremely low power and fast analog to digital converter.

NP-Invited On Demand-7 Seeing the Hidden Interface: Revealing Nanoscale Mechanisms of Contact, Adhesion, and Friction by *in situ* Experiments*, Robert Carpick,* University of Pennsylvania **INVITED**

Richard Feynman, in his famous and visionary 1959 lecture "There's Plenty of Room at the Bottom", included discussion of the ways in which friction, wear, and lubrication would be different at small scales. It is now well understood that, as technology scales shrink, tribological interactions – friction, adhesion, and wear – play increasingly dominant roles. This can be problematic (e.g., extremely high friction that prevents motion), or can offer solutions (e.g., using adhesion to drive the formation and stability of nanostructures). The biggest challenge in exploring and exploiting these scientific and technological issues is that the interface between two materials is hidden from view. Recently, advances in *in situ* methods have enabled tribological mechanisms at previously inaccessible interfaces to be studied with unprecedented resolution and insight. We will discuss the application of two *in situ* experimental methods to develop new, physically-based insights into tribological processes.

I will first discuss using a novel method based on atomic force microscopy (AFM) to study the formation of anti-wear tribofilms derived from additives present in lubricating liquids. These films are crucial for protecting contacting, sliding parts in machinery from damage by forming during use. AFM is conducted in additive-containing oils to monitor the growth, morphology, and physical properties of tribofilms *in situ* during sliding of a well-defined single asperity contact geometry. We show that the famous molecule zinc dialkyldithiophosphate (ZDDP) functions via surface-based nucleation, growth, and saturation of ZDDP antiwear tribofilms as a function of sliding time. Based on these results, a mechanism for explaining the mysterious self-limiting growth of these films is proposed. We also show that 5 nm diameter zirconia nanoparticles dispersed in a lubricant can also form protective films on surfaces, opening a pathway for more environmentally-friendly additives that can enable energy-saving low viscosity lubricants.

We will then discuss new insights into nanoscale adhesion and wear[1] achieved using *in situ* transmission electron microscopy (TEM) wear tests. For silicon, diamond, and diamondlike carbon, we observe different modes of wear, all distinct from classic wear models. We also see a strong, reversible, sliding-history dependence of adhesion between silicon nanoasperities, attributed to shear-induced removal of adsorbates. Finally, I will preview new results applying the technique to the study of contact between two-dimensional materials including MoS_2.

Nanoscale Science and Technology Division
Room On Demand - Session NS-Contributed On Demand

Nanoscale Science and Technology Contributed On Demand Session

NS-Contributed On Demand-1 Precision Control of Cavity Quantum Electrodynamics in Space-Time with fsTHz-STM, ***Likun Wang***, *Y. Xia, W. Ho,* University of California Irvine

Cavity quantum electrodynamics (QED) for a molecular two-level system interacting with quantized terahertz photons has been realized by combining a femtosecond THz laser with a low temperature scanning tunneling microscope (fsTHz-STM). A hydrogen molecule adsorbed in a Cu2N island grown on the Cu(100) surface and under the STM tip develops a dipole moment, becoming a two-level system in a double-well potential. A Stark effect is measured from the electric field by changing the junction bias. Time domain measurements by varying the delay of the pump-probe THz pulses reveal the coherent superposition of the two-level states. By decreasing the tunneling gap, the strong coupling regime is reached, leading to cavity-QED of the superposition of a single photon with the two-level states of a single hydrogen molecule within the STM junction cavity of sub-nm dimensions. An avoided crossing is observed as a function of the junction electric field in the transition from the ground state to the doublet superposition states. The photon-molecule coupling strength is directly obtained from the energy gap at the minimum of the avoided crossing. By tuning the tunneling gap and tip position with sub-Ångström precision, the coupling strength has been increased from zero to 25% of the energy separation of the two-level states. These results demonstrate electric control of the THz induced transitions to the superposition of photon-molecule cavity-QED states, enabled by measurements with simultaneous spatial and temporal resolutions, and suggest the use of molecules as qubits and carriers of quantum information.

NS-Contributed On Demand-4 RF Plasma for the Facile Fabrication of Bio-Functional Polymeric Nanoparticles, ***Laura Haidar***, University of Sydney, Australia

Multifunctional polymeric nanoparticles have advanced the field of nanotechnology, particularly biomedicine, by introducing a promising platform for targeted delivery, diagnostics, and therapeutics.Their surfaces can be conjugated with ligands such as proteins, peptides, pDNAs, fluorescent markers and drugs for versatile applications ranging from site-specific targeting, to bioactive delivery, cancer therapy, bioimaging and topical immunization. Conventionally, the functionalization of polymeric nanoparticles incorporates tedious wet-chemical processes that require multi-step protocols with high-cost disadvantages. Plasma polymerized nanoparticles (PPNs) produced through a simple, dry low-pressure plasma process can attain tunable radical-rich platforms that enable the direct attachment of ligands. In this study, we explored a C2H2/N2/Ar plasma as a rapid and cost-effective source to fabricate highly reactive particles capable of being functionalized with bio-active molecules. The discharge was generated by capacitively coupling the rf power (f = 13.56 MHz) to the plasma and is characterized along with the physical and chemical surface properties of the synthesized nanoparticles.

NS-Contributed On Demand-7 Mechanical Size Effect of Nanoconfined Polymer Films, ***Guorui Wang***, *F. Najafi, K. Ho, M. Hamidinejad, T. Cui, G. Walker, C. Singh, T. Filleter,* University of Toronto, Canada

The mechanical properties of polymer thin films are of scientific and technological interest to diverse communities of researchers. This interest is mainly driven by the development of flexible and stretchable electronics with a wide range of applications in flexible, wearable, and implantable devices. While the moduli of thin polymer films are known to deviate dramatically from their bulk values, the nature of such a size effect still remains debatable. Specially, indentation technique gives rise to contradicting results from both buckling experiments and molecular dynamics calculations, which is claimed to result from the substrate effect. Herein, we perform atomic force microscope (AFM)-based deflection testing on freestanding ultrathin polymethyl methacrylate (PMMA) films in confined geometry and demonstrate a significant mechanical stiffening behavior in the absence of substrate effect. Through a combination of small-angle X-ray scattering (SAXS) and scanning near-field optical microscopy (SNOM) measurements, a transition in chain conformations was identified from bulk to ultrathin film which can be directly related to the mechanical behavior of the polymer films. Based on such a structure-property relationship, we advocate that individual chains play a critical role in polymer mechanics at the nanoscale. Molecular dynamics (MD) modeling further unveils the dominance of entropic contribution over enthalpic contribution to the chain stiffness, in terms of substantial conformational transition but limited backbone straining during the stretching, which endows polymer films with higher load bearing capacity and accounts for the stiffening of polymer films. In this context, stress states of chains account for the molecular origin of the mechanical size effect of polymer thin films. In particular, biaxial stretching of chains (e.g. from the AFM deflection test) leads to the stiffening due to the chain stiffness effect, while the compression/bending (e.g. from the wrinkling method) results in a softening behavior in terms of the flexibility of chains. In contrast to the conventional interchain interaction-dominated elasticity mechanism, such a mechanistic understanding resolves the long-standing issue regarding the discrepancy in the observation of thickness dependent modulus of polymer thin films.

NS-Contributed On Demand-10 In-Plane Mechanical Properties of 2D Hybrid Organic-Inorganic Perovskites Nanosheets by AFM Nanoindentation, ***Doyun Kim,*** Texas A&M University*; E. Vasileiadou, I. Spanopoulos, M. Kanatzidis,* Northwestern University*; Q. Tu,* Texas A&M University

In-plane mechanical strains are commonly found in 2D metal halide organic-inorganic perovskites (2D HOIPs) which have attracted substantial interests due to their chemical/structure versatility and high-performance optoelectronic applications such as solar cells, light emitting diodes and flexible electronics. Such mechanical strain in HOIPs due to thermo-mechanical, electro-mechanical or photo-mechanical coupling derives the delamination and fracture of the functional materials, resulting in catastrophic failure of the devices. In order to mitigate these strain-induced stability issues, it is crucial to understand the fundamentals of mechanical properties and their relationship to the composition and structure of the material. However, the current understanding of the in-plane mechanical properties of 2D HOIPs and the influence of their structure on the mechanical performance is limited. Here, we employed Atomic Force Microscope (AFM) indentation to stretch suspended 2D lead halide Ruddlesden-Popper HOIP nanosheets, systematically studying the in-plane Young's moduli $E_{//}$. The general formula is $(R\text{-}NH_3)_2PbX_4$ where X = I, Br, or Cl and $R\text{-}NH_3$ is linear alkyl ammonium spacer molecule ($C_mH_{2m+1}\text{-}NH_3^+$, m = 4, 6, 8 or 12). With fixing the spacer molecule to butylammonium and varying halide ions, we found that the $E_{//}$ follows the trend of Pb-X bond strength (Pb-Cl > Pb-Br > Pb-I), which is different from that found in out-of-plane moduli $E_\perp$ of HOIPs, but rather closer to that found in 3D counterparts. Moreover, the impact of the alkyl ligand chain length on $E_{//}$ exhibits nonmonotonic dependence that decreases first and slightly increases again. This is likely due to the competition between the relative packing density of soft organics and the interfacial mechanical coupling associated with the packing of the alkyl chains. The mechanical anisotropy of 2D HOIPs can be tuned over a wide range ($0.1 < E_{//}/E_\perp < 2$) by engineering the organic spacer molecules, especially for the iodide-based 2D HOIPs, which is significantly different compared to other inorganic 2D materials. Our results provide valuable insights into the structure-property relationship regarding the mechanical anisotropy and in-plane mechanical behaviors of 2D HOIPs, which can guide the materials design and device optimization to achieve required mechanical performance in 2D HOIP-based applications.

NS-Contributed On Demand-13 How does Humidity affect the Mechanical Behavior of Halide Perovskites?, ***Isaac Buchine***, Bar-Ilan University, Israel*; I. Goldian, S. Cohen, D. Cahen,* Weizmann Institute of Science, Israel

ABX_3 Halide Perovskites, HaPs, where A= Methylammonium (MA), Formamidinium (FA), or Cesium (Cs), B= Pb, X=Chloride (Cl), Bromide (Br), or Iodide (I), are promising materials for the next generation of semiconductor-based devices. Their facile fabrication alongside intriguing optoelectronic properties make them outstanding candidates for incorporation into a variety of next generation technologies.

The effect of humidity on HaP *optoelectronic properties* has been investigated thoroughly, but no studies exist on how it influences their *structural and mechanical integrity*, critical, because of the apparent central role of their mechanical softness for their other properties. In particular, the well-studied HaP out-of-plane mechanical properties, are known to depend strongly on the Pb-X bond, but the influence of humidity on this characteristic has been ignored until now. This presents a difficulty in engineering devices containing these materials meant to operate under a range of ambient conditions.

We examined single crystals of five HaPs, MAPbX$_3$ (X = Cl, Br, and I) and APbBr$_3$ (A = Cs and FA), to elucidate the role composition plays in the humidity-dependent mechanical properties. A dedicated nanoindenter, as well as an atomic force microscope-based approach, were used to measure elastic and plastic deformation under varying *in situ* humidity conditions. Furthermore, using temperature-dependent desorption we identified a tightly bound water species populating about one in eight unit cells in a FAPbBr$_3$ crystal which was stored in dry conditions.

Our results reveal that the elastic modulus (E) increases by 4-10% while the hardness (H) decreases by 25% when RH (relative humidity) is increased from 10% to 60%. This effect is reversible upon reverting to the dry state. The phenomenon is strongest in HaP crystals with cubic lattices (MAPbCl$_3$, MAPbBr$_3$, and FAPbBr$_3$). HaP crystals with tetragonal lattices (CsPbBr$_3$ and MAPbI$_3$) show negligible humidity dependence relative to experimental uncertainty. This suggests that lattice structure and dimensions play a critical role in the humidity-HaP relationship, an aspect not usually taken into consideration when discussing the function of these materials.Common knowledge in the field suggests that H-bonding is the primary source for humidity effects on HaP properties. However, our research suggests that the lattice that is stable at RT and atmospheric pressure and the available space within the unit cell affects these properties as well, and should be considered.

NS-Contributed On Demand-16 Ultrathin, Stress-Free, Doubly-Clamped Nanomechanical Resonator*, **Jian Zhou**, N. Moldovan, L. Stan, H. Cai, D. Czaplewski, D. López,* Argonne National Laboratory

Ultrathin mechanical structures are ideal building platforms to purse the ultimate limit of nanomechanical resonators for applications in sensing, signal processing and quantum physics. As the thickness of the vibrating structures is reduced, the built-in stress of the structural materials plays an increasing role in determining the mechanical performance of the devices. Therefore, it is very challenging to create resonators working in the modulus-dominant regime, where their dynamic behavior is exclusively determined by the device geometry. Here we demonstrate the realization of ultrathin (nm thickness), high-aspect-ratio (L/t up to 5000), doubly-clamped nanomechanical resonators, with built-in stress in the kPa range. We show that the resonators have stiffness that scales with the device dimensions according to beam theory, as opposed to the magnitude of the built-in stress characteristic to a string. We observed room temperature thermomechanically induced motion more than ten vibrational modes with all the frequencies matching the calculations according to the beam theory, and a record frequency tuning range of more than 50 times by the application of ~1x10^{-3} strain while retaining simple harmonic response of the resonator. These results illustrate a new strategy for the quantitative design of nanomechanical resonator with unprecedented performance.

NS-Contributed On Demand-19 Thermal Activation of Nanoscale Wear*, W. Wang,* Southwest Jiaotong University, China*; D. Dietzel, **Andre Schirmeisen**,* Justus-Liebig University Giessen, Germany

Macroscopic wear is routinely described by empirical laws like, e.g., the historic Archard's law, while the underlying microscopic processes are still under scientific debate. On the nanoscale the removal of single atoms from the sliding surfaces is considered the most fundamental mechanism of wear, also termed atomic attrition. Especially atomic force microscopy (AFM) techniques have been widely used to explore nanoscale wear in single asperity sliding scenarios, where material abrasion can be found for both the AFM tip and the substrate depending on the experimental conditions or material combinations.

In this work we have created nanoscale wear tracks on ionic crystals by reciprocating single asperity scratch tests using AFM. The wear characteristics are analyzed by the scratch depth as a function of surface temperature from 30 to 300 K. We find two distinct regimes of wear track formation: At low temperatures the wear groove volume shows a monotonic increase with contact time and temperature, fully consistent with the thermally activated Arrhenius kinetics. Above a certain temperature threshold, however, the wear tracks start to show a periodic wear pattern and the total wear volume becomes almost independent of temperature. This apparent contradiction can be understood if further competing processes are considered at high temperatures. These include surface diffusion and rebonding processes of the atomic wear debris, previously shown to be responsible for the formation of quasiperiodic mound patterns. Finally, we show that with a proper wear mound volume correction even the high temperature wear data can be described by the simple Arrhenius model, indicating that the same atomic attrition process is responsible in both regimes. By linking these two regimes, our results hint at a path to predict nanoscale wear not only for smooth but also for rough surfaces, a further step toward realistic interfaces.

NS-Contributed On Demand-22 Reduction in Contact Time of Bouncing Droplets on Compact Nanostructured Superhydrophobic Surfaces*, **Lin Wang**,* Department of Materials Science and Engineering, Materials Research Institute,The Pennsylvania State University, University Park*; T. Wong,* Department of Mechanical Engineering, Materials Research Institute, The Pennsylvania State University, University Park

Many natural surfaces are capable of shedding water droplets rapidly, which has been attributed to the presence of low solid fraction (Φ_s~ 0.01) according to the classical wetting theories. However, recent high-resolution microscopic observations revealed the presence of unusual high solid fraction nanoscale textures on water-repellent insect surfaces. For example, superhydrophobic mosquito eyes, springtails, and cicada wings possess solid fractions (Φ_s) as high as 0.25 – 0.64. In addition, the texture size on these insect surfaces is typically on the order of 100 – 300 nm. To understand why both high solid fraction and nanoscale textures are important for these superhydrophobic insect surfaces, we systematically designed and fabricated a series of textured surfaces with texture size varying from 100 nm to 30 µm at solid fractions of 0.25 and 0.44, and investigated their static and dynamic wetting behaviors. Here we show that the contact time of bouncing droplets on high solid fraction surfaces can be reduced by reducing the texture size to nanometer scale. Specifically, we discovered that high solid fraction surfaces (Φ_s ~ 0.44) with texture size ~100 nm could reduce the contact time by ~2.6 ms compared to that with texture size >300 nm. This texture-size dependent contact time reduction on solid surfaces has not been observed previously, and cannot be explained by existing surface wetting theories. We showed theoretically that the reduction in droplet contact time can be attributed to the dominance of three-phase contact line tension on compact nanoscale textures. Through pressure stability analysis and experiments, we have further shown that high solid fraction (Φ_s> 0.25) is an important requirement for insects to withstand high-speed impacting raindrops. Our results suggest that the compact and nanoscale textures on water repellent insect surfaces may work synergistically to repel and shed impacting raindrops rapidly, which could be an important survival strategy for flying insects. Technologically, the ability of compact nanoscale textured materials to repel high-speed impact of liquid droplets with reduced contact time may find use in a range of applications including fouling-resistant personal protective equipment (PPE) to insect-sized flying robots and miniaturized drones.

Keywords: contact time | drop impact | insects | nanoscale textures | pressure stability | superhydrophobic surfaces

NS-Contributed On Demand-25 Efforts of Interlayer Interaction on van der Waals Heterostructure Nanomechanical Resonators*, **Wen Sui**, J. Lee, P. Feng,* University of Florida

Atomically thin membranes made of two-dimensional (2D) layered materials such as graphene and molybdenum disulfide (MoS$_2$) have attracted considerable interests in enabling novel resonant nanoelectromechanical systems (NEMS) thanks to their superior mechanical properties (*e.g.*, high Young's modulus, E_Y≈200 GPa-1TPa, and ultrahigh strain limit, often up to $\varepsilon_{\text{limit}}$≈25%). Various 2D NEMS resonators based on different crystalline materials have been demonstrated with great performance, including wide frequency tuning up to $\Delta f/f_0$≈1300%[1] and broad dynamic range up to ~110dB[2].

Recently, van der Waals heterostructures based on stacking of atomically thin 2D crystals with disparate electrical, mechanical, and thermal properties have been proposed for the realization of new functional NEMS devices. Previous work in MoS$_2$/graphene heterostructure NEMS resonator indicates that the resonance frequencies and *Q* factors of the heterostructure 2D resonators lie between the values of single-material resonastors in graphene or MoS$_2$[3]. In such 2D heterostructures, interlayer slip may occur owing to the effects of twist, strain, or mismatch of lattice constants[4]. However, how the interlayer interactions affect the tension level, thermal expansion, and damping of heterostructure resonators is elusive and unexplored so far.

In this work, we investigate the performance of 2D NEMS resonators enabled by atomic layer MoS$_2$/graphene van der Waals heterostructures with respect to temperature variations by using finite element method (FEM) simulations.We mainly focus on exploring the effects ofstress softening, geometric changes, as well as the temperature dependence of material properties. Effects of thermal cycling on the interlayer interactions, especially how the interfacial bonding and/or the thermal expansion affect the nanomechanical characteristics of suspended MoS_2/graphene resonators are systemically analyzed. This work opens possibilities for studying multi-physical coupling effects in 2D heterostructure devices by unraveling the interlayer interactions in van der Waals heterostructures.

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NS-Contributed On Demand-28 Intrinsic and Interfacial Fatigue of Graphene*, Teng Cui*, *T. Filleter,* University of Toronto, Canada

The booming applications of graphene in flexible electronics, mechanical structures, and biomedical sensors require robust mechanical and structural properties as a premise. With the ever-increasing demand for the long-term reliability of graphene-based devices and structures in real applications, the fatigue behavior of graphene necessitates careful investigation, especially its intrinsic fatigue behavior and interfacial fatigue behavior at contact. The fatigue concern of graphene is more stringent under extreme loading conditions for more complicated designs, such as at severe stress concentrations and abundant interfaces in flexible devices. Here we enabled the intrinsic fatigue study of suspended two-dimensional (2D) materials based on a modified atomic force microscopy technique. We discovered [1] that monolayer and few-layer graphene also suffered mechanical fatigue, but they exhibited remarkable fatigue life of more than one billion cycles at large stress levels (e.g., at σ_{mean}=71 GPa and $\Delta\sigma$=5.6 GPa), which is higher than any materials reported to date. Surprisingly, monolayer graphene did not reveal any obvious progressive damage during cyclic loading, as manifested by its non-changing morphology and non-degraded mechanical properties, as well as atomic structures examination by molecular dynamics simulations. Graphene oxide, meanwhile, also exhibited ultrahigh fatigue resistance, but revealed clear progressive damage, similar to conventional fatigue mechanisms. Despite the record-high intrinsic fatigue life of graphene, we observed significant interfacial fatigue damage when introducing graphene-polymer contact [2]. The significant elastic mismatch and weak van der Waals (vdW) interactions at the interface resulted in the generation and propagation of graphene buckles, which was revealed to follow an inverse Paris' law. Moreover, cyclic loading through the vdW interfaces could also induce fracture of graphene even in tens of cycles, with the main fracture modes identified as in-plane shear at the fold junctions and tear. These studies provide fundamental insights on the dynamic reliability of graphene and call for further fatigue studies of other 2D materials and their interfaces.

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NS-Contributed On Demand-31 Atomic-Scale Visualization of Electron-Pair Fluids and Crystals*, Xiaolong Liu,* *Y. Chong,* Cornell University*; R. Sharma,* University of Maryland College Park*; J. Davis,* Cornell University/University of Oxford/University College Cork

Translationally invariant electron pair fluids exist inside most conventional superconductors. However, electron pairs can also form crystalline states such as pair density waves (PDWs) that break translational symmetry. Experimental evidence of PDWs remains scarce due to the difficulty in directly visualizing the superconducting condensate. Herein, using atomic-resolution scanned Josephson-tunneling microscopy (SJTM), we show that PDW states exist in transition metal dichalcogenides, here $NbSe_2$. Enabled by SJTM, we further visualized the velocity field and supercurrent density of a flowing electron-pair fluid on the surface of $NbSe_2$. Such techniques are expected to find broad applications in other emerging quantum materials.

NS-Contributed On Demand-34 High-Speed Scanning Tunneling Spectroscopy*, Hamed Alemansour*, *S. Moheimani,* University of Texas at Dallas*; J. Owen, J. Randall, E. Fuchs,* Zyvex Labs

Scanning tunneling microscope (STM) has been extensively used as an atomic-scale spectroscopy tool. One STM spectroscopy technique is current-imaging tunneling spectroscopy (CITS), i.e., recording I-V or dI/dV curves for every pixel of a topographic image. This offers a route to extract local electronic properties of surfaces. Implementation of CITS requires negligible lateral drift, low measurement noise, and a highly stable tip-sample junction. These requirements impose significant technical hurdles to increase the speed and precision of this technique and a map of a small area can take hours to be completed.
We present a novel method to obtain I-V spectra for every pixel of an image under normal imaging speeds. Unlike the conventional approach, where the feedback loop is disconnected for every pixel and then the bias voltage is ramped over the desired range to record the tunneling current, we have developed a method to obtain I-V curves without the need to interrupt the feedback loop. Experimental requirements for this scanning tunneling spectroscopy (STS) method are easily fulfilled at room temperature. In this approach, a high-amplitude sinusoidal modulation voltage without a dc bias is generated by a lock-in amplifier and is applied to the sample. The resulting current that contains both tunneling and capacitive components is then amplified by a high bandwidth preamplifier. This is then sent to the lock-in amplifier that measures in-phase (a_1) and 90° out of phase (b_1) components of the current with the modulation signal. The natural logarithm of a_1 ($\ln(a_1)$) is compared with a set-point value and the error signal is sent to the controller. Similar to the constant current imaging mode, a topographic map of the sample is constructed by plotting the controller output along with the in-plane position of the tip. The tunneling current is also obtained by subtracting the capacitive current from the total current and I-V curves are constructed for every pixel, simultaneously with the imaging. This enables us to obtain a spectroscopic map of the surface hundreds of times faster than the conventional CITS method.

NS-Contributed On Demand-37 Phonon Polaritons in New Materials for Nanophotonic Applications*, Vanessa Breslin,* *D. Ratchford,* U.S. Naval Research Laboratory*; A. Giles,* Quantitative Scientific Solutions, LLC*; A. Dunkelberger, J. Owrutsky,* U.S. Naval Research Laboratory

Phonon polaritons are collective nuclear charge oscillations resulting from the coupling of photons with optical phonons in polar materials and are supported within a material-specific spectral region called the reststrahlen band, which is bounded by the transverse and longitudinal optical phonons. In this region, the material behaves optically like a metal; it is highly reflective and has a negative real part of the permittivity. When polar materials are nanostructured, phonon polaritons can enable a variety of near-field optical effects such as sub-diffraction light confinement. Interestingly, a polar material which supports phonon polaritons can also have anisotropic optical properties, such that different components of its permittivity tensor have opposite signs. These materials are referred to as hyperbolic since, within the reststrahlen band, they behave optically like a dielectric and a metal along different crystal axes. Here, we report on the first observation of hyperbolic phonon polaritons (HPs) in calcite nanopillar arrays, demonstrate the aspect ratio dependence of the HP resonance frequencies, discuss fabrication challenges, and compare our results to numerical simulations and analytical models. Additionally, our efforts toward using calcite to demonstrate surface enhanced infrared absorption (SEIRA), a useful technique for chemical sensing applications, will be presented. Although plasmonic materials can be used for SEIRA, these materials typically suffer from high optical losses due to the fast scattering of electrons, which results in broad optical resonances. In contrast, phonon polaritons have much lower optical losses because of the slower scattering rates of phonons, resulting in narrower resonance bands. Therefore, calcite is an ideal low-loss material for studying HPs that could find applications in mid-IR nanophotonic devices, and these results pave the way for expanding the type of materials that support phonon polaritons.

NS-Contributed On Demand-40 Nanoscale Chemical Analysis of Heterogeneous Amphiphilic Surfaces via Photo-Induced Force Microscopy*, Derek Nowak*, *P. O'Reilly,* Molecular Vista*; J. Benda, C. Gu, D. Webster,* North Dakota State University*; S. Park,* Molecular Vista

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-10 nm spatial resolution).The exceptional spatial resolution is due to the tip-enhanced near-field profile, which extends ~ 10 nm into the sample surface. In this talk, we present a slightly modified PiFM configuration where the technique becomes more bulk sensitive, which when combined with the surface-sensitive PiFM mode, allows a nanoscale "3-dimensional" analysis of a heterogeneous material system.We demonstrate the elegance and utility of the technique by analyzing amphiphilic siloxane-polyurethane (AmSi-PU) coatings, which have shown excellent fouling release properties due to the lateral phase separation and vertical stratification of the different constituent polymers [2]. The conclusions that are drawn from the PiFM measurements are compared with the conclusions that are drawn from multiple other techniques, which included ATR-FTIR, XPS, and AFM.

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NS-Contributed On Demand-43 Controlled Electron-Induced Fabrication of Metallic Nanostructures on 1nm Thick Carbon Nanomembranes*, C. Preischl,* Friedrich-Alexander Universität Erlangen-Nürnberg, Germany*; **Linh Hoang Le**,* Universität Bielefeld, Germany*; E. Bilgilisoy,* Friedrich-Alexander Universität Erlangen-Nürnberg, Germany*; F. Vollnhals,* PFriedrich-Alexander Universität Erlangen-Nürnberg, Germany*; A. Gölzhäuser,* Universität Bielefeld, Germany*; H. Marbach,* Friedrich-Alexander Universität Erlangen-Nürnberg, Germany

Metallic nanostructures deposited on 2D materials are increasingly desirable for many electronic, magnetic and optical applications. Focus electron beam induced deposition (FEBID) is a direct and maskless lithography technique that operates based on irradiating precursor molecules by a focus electron beam of an electron microscope to dissociate them locally and then leave a metallic deposit.[1][2][3] Taking advantages of this technique, we could write highly pure iron patterns on a terphenylthiol self-assembled monolayer (SAM) with controlled shapes and sizes. Consequent crosslinking of the SAM under a low energy electron beam results in an insulate carbon network, which is well-characterized and known as carbon nanomembrane (CNM)[4]. This 1 nm thick membrane can be transferred on tertiary solid substrates, for example SiO_2, or freely suspended on TEM grids, while the iron nanostructures are well preserved. This work has illustrated that the combination of FEBID and CNMs can be a promising route to obtain various metallic nanostructures with arbitrary designs embedded on mechanically stable and flexible ultrathin films.

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NS-Contributed On Demand-46 Fully Motorized, Tip-Scanning AFM With Photothermal Excitation for Improved Imaging and Cell Measurement Methods*, Jonathan Adams*, *C. Bippes, L. Howald, S. Fricker, P. Frederix, P. van Schendel, H. Gunstheimer, L. Gonzalez, G. König,* Nanosurf AG, Switzerland*; G. Fläschner,* ETH Zurich, Switzerland*; D. Ziegler,* Nanosurf AG, Switzerland

Atomic force microscopes (AFMs) are versatile tools that can effectively resolve structures and probe mechanical properties at length scales from nanometers to tens of micrometers, and in environments ranging from vacuum to biological solutions. Nevertheless, there is a strong continued need for AFMs with improved ease of use, reliability, and integration with complementary techniques. Recently, we have developed a new instrument, the DriveAFM, that combines a unique set of technological features for improved performance and ease of use. These include a tip scanning architecture that allows for flexibility over sample size and seamless integration with optical microscopy, fully motorized optomechanical adjustment that permits automation of many routine instrument adjustments as well as remote operation, and photothermal excitation that excites cantilever oscillations in a straightforward and stable manner independent of environment.

In this work, we will illustrate how a novel optical guiding architecture overcomes the engineering challenges involved in incorporating these technological features in a tip scanning AFM. Our architecture allows for removing most optomechanical components from the scanner [1]. We will also highlight a range of new measurement and imaging modes that are enabled specifically through the incorporation of photothermal excitation. In comparison with piezoacoustic excitation, photothermal excitation can cleanly actuate the cantilever over a wide bandwidth of frequencies without influence of the surrounding environment or support structure [2]. The resulting clean phase response of photothermally-excited cantilevers allows for more accurate tracking of the cantilever resonance frequency, used in the PicoBalance technology which enables fast and accurate measurements of cell and particle mass [3]. Furthermore, direct off-resonance actuation of cantilever deflection through photothermal excitation allows for cell mechanical property measurements at a wide range of frequencies [4], and off-resonance imaging modes that run at higher detection frequencies in comparison with previous piezo-based approaches [5].

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NS-Contributed On Demand-49 Effect of the Surroundings on the Controlled Manipulation of Individual Phenyl Groups*, Omur Dagdeviren*, *C. Zhou, E. Altman, U. Schwarz,* Yale University

Scanning probe microscopy has made it possible to move molecules between surface sites at will while quantifying the potential energy barriers along the manipulation path as well as the energy landscape surrounding the molecule in its initial and final positions. To explore the practicality of these abilities as a novel pathway to exploring the interactions between molecules as bonds form and break in a catalytic cycle, we selected iodobenzene molecules on a Cu (100) surface as a model system. To this end, we first break the iodine atom from the benzene ring by applying a controlled bias voltage to form a phenly group. Afterwards, a manipulation path is chosen along which the tip moves at constant but continuously reduced heights while recording the oscillation amplitude and phase phi with the microscope operated in our recently developed tuned-oscillator (TO) detection scheme [1]. To preserve the accuracy of recovered tip-sample interaction potentials and forces, we use oscillation amplitudes significantly larger than the decay length of the tip-sample interaction potential [2,3]. Here, we show how moving a phenyl away from the iodine atom reduces the energy barrier required to initiate motion with increasing distance, thereby disclosing the effect of local surface chemistry.

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NS-Contributed On Demand-52 Atomic-Scale Study of the Degradation Process on Single-Crystal Perovskite Surfaces: From Ultra-High Vacuum to Ambient Pressures*, Joong Il Jake Choi*, Center for Nanomaterials and Chemical Reactions, IBS, Republic of Korea*; M. Khan,* School of Electrical Engineering, KAIST, Republic of Korea*; Z. Hawash,* Energy Materials and Surface Sciences Unit, OIST, Japan*; K. Kim,* Beamline Research Division, Pohang Accelerator Laboratory (PAL), POSTECH, Republic of Korea*; H. Lee,* Department of Chemistry, KAIST, Republic of Korea*; L. Ono, Y. Qi,* Energy Materials and Surface Sciences Unit, OIST, Japan*; Y. Kim,* School of Electrical Engineering, KAIST, Republic of Korea*; J. Park,* Center for Nanomaterials and Chemical Reactions, IBS, and Department of Chemistry, KAIST, Republic of Korea

While organic-inorganic hybrid perovskites are emerging as promising materials for next-generation photovoltaic applications, the origins and the pathways of the instability of perovskites remain speculative. Herein, we employ ambient-pressure atomic force microscopy (AP-AFM) and ambient-pressure x-ray photoelectron spectroscopy (AP-XPS) to carry out surface characterization and atomic-scale analysis of the reaction mechanisms for methylammonium lead bromide ($MA(CH_3NH_3)PbBr_3$) single-crystal surfaces in environments ranging from ultra-high vacuum (UHV) to ambient pressures. $MAPbBr_3$ single crystals grown in a solution process are mechanically cleaved at UHV to obtain an atomically clean surface. We observe surface inhomogeneity on the freshly cleaved $MAPbBr_3$ surface: the coexistence of MA-terminated layers with cubic layer heights, and full and partial coverage of $PbBr_2$-terminated defective layers with lower layer heights. Consecutive topography and lateral force measurements in low pressure water ($p_{water} \approx 10^{-5}$ mbar) show the creation of degraded patches that are one atomic layer deep, gradually increasing their coverage until fully covers the surface at water exposure of 2×10^6 Langmuir. We observed high-friction perimeters of the degraded patches which are equivalent to MABr-flat surface where methylammonium ligand establish strong interaction to the AFM tip, enhancing local friction. We show that exposure to high pressure water (p_{water} = 0.01 mbar) depletes the organic ligands from the surface of $MAPbBr_3$, which leads to the formation of $PbBr_2$ clusters and Br-rich surface.

NS-Contributed On Demand-55 Correlative Imaging With Chemical Identification and Mechanical Mapping at the Nanometer Scale*, Shuiqing Hu*, *M. Wagner, W. Wang, H. Mittel, C. Su,* Bruker Nano Surfaces Inc

Mid IR induced photothermal effects at the nanoscale established an unique method for nanoscale chemical characterization and identification. Combining with PeakForce Tapping™ mode, PeakForce™ IR have demonstrated as an effective method to achieve high resolution chemical mapping. However, due to interaction time limited by PeakForce Tapping™ duty cycle, the photothermal IR detection has a lower efficiency comparing to contact mode and Tapping™ AFM IR. In this paper, we discuss a new method significantly improving S/N using multiple pulse train synchronized to the peak force interaction timing. Instead of the traditional single pulse trigger, a multi pulse train excitation is deployed, causing responses of the high Eigen mode contact resonance of the cantilever. Photo-thermal induced PeakForce™ IR signal can be enhanced by the much increased quality factor of the high Eigen mode contact resonance. High frequency for these contact resonances also facilitates more pulses for each tip-sample interaction cycle, leading to higher efficiency excitation of the photothermal IR signals. With combined efforts, the S/N can be improved by more than a factor of 2. Additionallywe have developed correlative imaging with simultaneous chemical identification and nanomechanical mapping at the nanometer scale. The value of these correlative imaging are demonstrated in various inhomogeneous materials with diverse mechanical properties.

NS-Contributed On Demand-58 High-Speed Scanning Ion Conductance Microscopy (SICM) for Imaging Cellular Process*, Georg Fantner*, *S. Leitao, B. Drake, V. Navikas, A. Radenovic,* EPFL, Switzerland

Scanning ion conductance microscopy (SICM) is a non-invasive scanning probe technique where the topography of the sample surface is sensed via the flow of ions through a nano-capillary. This technique is particularly well suited for very soft samples such as living mammalian cells. As such, SICM would be ideal for time-lapse investigations of stemcell differentiation, virus infection, or membrane trafficking. However, traditionally SICM is a very slow technique, requiring hours for high-quality imaging. Based on techniques originally developed for high-speed AFM, we have built a high-speed SICM that increased the hopping rate by a factor of 50 and can record images within seconds to minutes. Using a custom sample heater and perfusion chamber we can image live cells for 24h with high temporal resolution. The system is combined with a super-resolution optical microscope for correlative SICM/super-resolution fluorescence imaging. We use this system to study melanoma cell differentiation and its response to drug treatments.

NS-Contributed On Demand-61 Metasurface Lens Efficiency Improvement using Genetic Algorithm with Evolutionary Optimization*, David Czaplewski,* Argonne National Laboratory, USA*; H. Cai,* New York University*; S. Srinivasan, A. Martinson,* Argonne National Lab*; D. Gosztola,* Argonne National Laboratory, USA*; L. Stan, T. Loeffler, S. Sankaranarayanan,* Argonne National Laboratory*; D. Lopez,* national institue of Standards and Technology

Recently, metasurface lenses have drawn significant interest to replace macroscopic lenses in applications ranging from cellular phones to medical diagnostic equipment because of their extremely small footprint in the transmission direction. Metasurface lenses focus light by creating the phase profile similar to a Fresnel lens and typically follow two common designs: waveguide design and nanoparticle design. The waveguide design uses high aspect ratio structures to confine the light within the structure and create an effective index of refraction in a sub-wavelength region of the lens[1,2]. By varying the lateral dimensions of the waveguide, different phase delays can be created, while each waveguide remains independent from their neighbors. The primary problem with the waveguide design is that the creation of the high aspect ratio structures does not use commercially available processes. The nanoparticle design consists of an array of sub-wavelength dimension nanocylinders. The magnetic and electric dipole moments of the structure are tuned through lateral dimensions to match with the incident wavelength of light, creating an antenna, with full phase control from 0 to 2p and near 100% transmission. Using arrays of nanoparticles, phase delays can be characterized for different radii of the cylinders and spacing between cylinders. The fabrication process used to create the nanoparticles is CMOS compatible. The primary limitation of the nanoparticle design is that the nanoparticles interact with their neighbors. This complicates the design process. Borrowing the phase profile from a Fresnel lens and creating a nanoparticle metasurface, light can be focused to the desired focal point. However, the efficiency is low at 30%. Therefore, we employ an inverse design method[3] using a genetic algorithm (GA) with evolutionary optimization to design a lens that achieves an efficiency of 60% when fabricated and measured. In this talk I will present the fabrication of the metasurfaces and the methodology used to characterize the lenses. I'll also introduce the GA that we used to optimize efficiency. I'll discuss future directions of this work.

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NS-Contributed On Demand-64 THz Dynamics of Correlated Excitations in Moiré Superlattice*, Jun Xiao,* *C. Xia, A. Lindenberg,* Stanford University

The emerging twisted heterostructures based on 2D layered materials have opened a unique platform to explore exotic correlation physics and novel heterostructure optoelectronic devices at the atomically thin limit. The tunable Moiré potentials, arising from interlayer couplings, result in the emergence of various novel orderings such as Mott insulating phases, unconventional superconductivity, and Moiré excitonic phases. In particular, transition metal dichalcogenide heterostructures allow for optically-excited electrons and holes to reside in different monolayers and for trapping in the tens-of-meV Moiré potential, which is quite favorable for developing valleytronics, exciton condensation, and programmable quantum emitter arrays. Further progress along this direction requires a precise understanding of the formation of these Moiré excitons, and how such formation can be engineered by Moiré potentials and electron correlations.

Here we use ultrafast terahertz emission spectroscopy to probe interlayer charge transfer and other quasiparticle dynamics in several types of Moiré superlattice based on the transition metal dichalcogenides. With ultrafast visible and near-infrared laser pumping of these distinct Moiré superlattices, we observed nontrivial variations in the THz emission dynamics and spectroscopy. Experiments indicate such changes are closely associated with varying Moiré patterns and momentum mismatch conditions. Our findings advance the microscopic understanding of the correlated carrier formation dynamics in twisted heterostructures and hold great promise to advance the development of novel 2D optoelectronic devices.

NS-Contributed On Demand-67 Combined Scanning Gate Microscopy and Light Excitation Measurements on Semiconductor Nanowires*, Yen-Po Liu,* *J. Fast, Y. Chen, M. Kumar,* Lund University, Sweden*; R. Zhe,* DESY, Germany*; R. Timm, A. Burke, H. Linke, A. Mikkelsen,* Lund University, Sweden

InAs nanowires with tailored axial InP segments have attracted significant interest for nanophotonic applications such as photovoltaics, lasers and photodetectors as well as fundamental studies of for example hot-carrier dynamics [1,2,3]. Local variable electrical gating is very useful for studies of nanowires [4] and in conjunction with light excitation could explore the influence of local carrier density and band bending variations on device performance. This combination is however yet to be applied to nanowire devices. We have created a combined scanning photocurrent, atomic force and scanning gate microscopy (SPCM, AFM, SGM) setup to measure both local geometry and response to local light and voltage sources. We have used this setup to investigate the electronic response to local illumination and local gating response of InAs nanowires with/without an axial 25 nm InP segment.

The SGM imaging clearly show the influence of a local gate on the current profile of the InAs/InP nanowire devices. By placing the tip in specific positions on the wire, the current through the nanowire is enhanced by an order of magnitude. Simulations of carrier transport through the nanowire system as a function of gating tip position are performed based on drift-diffusion modelling [5] and the specific system geometry (from AFM images). A qualitative agreement between experiment and simulations is observed, which aids understanding of the device behaviour.When the nanowire is optically excited, significant changes in the SGM data are observed.These observations are discussed both in terms of carrier excitation in the wire, as well as the influence of surface states that can trap free carriers and introduce long-term memory effects in the devices. In conclusion, we show that by combining SGM, AFM, SPCM and simulations, new insights into the dynamics of nano-optoelectronic devices can be gained.

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NS-Contributed On Demand-70 Ultralow Friction of Magnetene, a non-van der Waals 2D Material

Peter Serles, University of Toronto, Canada; *A. Puthirath,* Rice University; *S. Yadav, C. Veer Singh,* University of Toronto, Canada; *P. Ajayan,* Rice University; *T. Filleter,* University of Toronto, Canada

Two-dimensional (2D) materials are known to create ultralow friction interfaces by reducing the energy dissipated during the sliding of a contact. While this is often attributed to van der Waals (vdW) bonding of 2D materials, it is known that nanoscale and quantum confinement effects can act to modify the atomic interactions of a 2D material producing unique interfacial properties. We demonstrate that the ultralow friction which is characteristic of graphene and other vdW materials can be achieved in magnetene, a non-vdW bonded 2D iron oxide (Fe_3O_4). Upon exfoliation from its bulk ore, the friction force of 2D magnetene as determined by friction force microscopy is found to decrease by a factor of more than 3 presenting statistically similar friction to common benchmark vdW materials. This effect, however, is unique to magnetene and is not present in the chemically similar 2D hematene (Fe_2O_3) or isostructural 2D chromiteen ($FeCr_2O_4$).

This ultralow friction can be attributed to nanoscale and quantum confinement of magnetene in producing three predominant mechanisms. First, the exfoliated (110) plane presents the lowest potential energy corrugation of the five materials as determined by DFT calculations. Using the potential energy corrugation to calculate the Prandtl-Tomlinson ideal friction of these materials shows considerable relative agreement with experimental friction values further validating this mechanism.[1] Second, quantum well confinement of a material to 2D can alter valence states and reactivity by electron confinement to 2D. It is noted by x-ray photoelectron spectroscopy measurements that magnetene shows a decrease in iron valence from $Fe^{2.66+}$ towards Fe^{2+} which corresponds with reduced frictionally-detrimental OH^- adsorbate compared to the other non-vdW 2D materials.[2] Third, forbidden phonon modes due to asymmetric soft surface bonding are noted in the Raman spectra of magnetene accompanied by a reduction in phonon modes parallel to the direction of sliding. Phononic friction is due to the damping of sliding energy by atomic collisions with parallel phonon modes[3] therefore the modified phonon modes of 2D magnetene lessen damping thus reducing the friction force.

These three mechanisms of exfoliation, quantum confinement, and asymmetric surface bonding all contribute to creating a nanomaterial with ultralow friction properties which does not rely on the vdWs nature of bonding. This study not only identifies the fundamental mechanisms for the appearance of ultralow friction in a non-vdW material, but also presents the starting point for the engineering of nanomaterial properties to produce optimized 2D material interfaces.

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NS-Contributed On Demand-73 Nano-Mechanical Characterization of Organic Micro-Inclusions in Flint

Sidney Cohen, *I. Rosenhek-Goldian,* Weizmann Institute of Science, Israel; *T. Corrales,* Technical University Federico Santa Maria, Brazil; *F. Natalio,* Weizmann Institute of Science, Israel; *A. Cernescu,* Neaspec, Germany

Flint is a siliceous sedimentary deep sea rock produced by marine bacterial activity within a chalky environment under anoxic conditions. During the rock formation process, bacteria are entombed inside a silica gel. Organic remnants are thus key to understanding the initial and subsequent environment of the rock, but are subject to degradation and percolation occurring over millions, or even billions of years. This greatly complicates attempts to glean information on the past biology and evolution of the organic content. Eocene flint is relatively young - 50 million years old - and despite the fact that its organic matter could give a hint at how organics in much older flint have evolved over the years, this aspect remains largely unstudied.

We have applied a combination of in-situ, nanocharacterization techniques to gain new insights on this problem. These efforts were directed toward organic micro-inclusions entrapped in the flint. In particular, we show that the mechanical response of this material is an important quantity that provides complementary and unique data amongst other nano-characterizations applied. The small size, thickness and irregular morphology of the organic micro-inclusions make it very difficult to accurately determine the mechanical properties. Such irregularities rendered nanoindentation measurements unreliable. Scanning probe-based contact resonance measurements, on the other hand, proved to be suitable and consistent for characterizing these inclusions. We found a value of 29 GPa for the storage modulus of the organic micro-inclusion, while modulus values for the surrounding stone, 78 GPa, were typical for flint. Independent techniques, including nano-IR, Tof-SIMS, micro-Raman and EDS analysis, hint at a proteinaceous material (amine IR peak), yet this modulus is surprisingly high for a protein species in (the spectroscopically-determined) alpha-helix conformation. The micro-inclusion was further studied by exposing it to liquid water, which caused measurable swelling, and a strong decrease of the modulus. Both of these changes were reversible upon dehydration. The modulus in this case was measured using peak-force quantitative mechanical measurement. In this talk, the correlation amongst these different types of data will be presented to derive a full picture of these ancient organic pools. Strongly relying on the data from the nanoscale measurements, we propose that the pool is consistent with proteins and a mixture of diagenetic products.

Here we present the application of quantitative scanning probe-based mechanical measurements on ancient organic pools found inside flint. Despite their small and irregular size, as well as the rough morphology of these inclusions, these measurements have proven to be valuable, in situ techniques for determining the mechanical characteristics of flint. This approach, based on a suite of nanoscale techniques including the first quantitative nanomechanical measurements in this specialized geological context, describes a fresh approach to a (very) old problem.

NS-Contributed On Demand-76 Mechanical Properties of Fibrillar Materials: The Role of H-Bond Formation in Amyloid Peptides

Irit Rosenhek-Goldian, *N. Aggarwal, D. Eliaz, H. Cohen, S. Cohen, A. Kozell , T. Mason , U. Shimanovich ,* Weizmann Institute of Science, Israel

The process of protein self-assembly into fibrillar structures generates the strongest biomaterials in the world, like silk fibers, but, unfortunately, is also associated with the development of neurodegenerative diseases.

Hydrogen bonds (H-bonds) are particularly important for proteins and natural peptides. They provide an organization guide for distinct protein folds, conferring stability to the protein structure and enabling specificity for selective inter- and intramolecular interactions.

Here, we describe a general approach for understanding the role of H-bonds in the protein self-assembly process on the fibril's exceptional mechanical properties. A series of peptides were studied in order to investigate the influence of substitution of an aliphatic amino acid by an aromatic one. These variations cause perturbations to the H-bonded network, that control the morphology and molecular structure of the formed fibers in a rational way.

Mechanical and morphological measurements conducted with AFM suggest that such changes severely affect the folds and fibrillation pathway in the mature solid state of the fibrils. This enables the manipulation of the end-point structure and the mechanical properties of fibrillar proteins, leading to Young's modulus alterations. When the peptides arrange in a globular structure they display relatively low modulus values of <7 GPa. fibrillar peptide assemblies show increased elastic modulus values ranging between 10 – 29 GPa,with the presence of aromatic amino acids contributing to improved stiffness. Amino-acid hydrophobicity and its propensity toward H-bond formation play a crucial role in the structural organization of peptide assemblies and in the rigidity of the formed structures. We show that steric hindrance, achieved via aliphatic-to-aromatic amino acid substitution, does not affect the natural propensity of the peptides to form amyloidogenic fibrils. These perturbations, however, do trigger changes in H-bonded network and conformational changes.These results are supported by structural and compositional analyses, electron diffraction, FTIR and quantitative XPS.

The approach presented here promotes a general understanding of the role of H-bonds in protein aggregation and opens the opportunity to utilize amyloidogenic protein fibrillation phenomena in rational material design.

NS-Contributed On Demand-79 A Novel Experimental Method for Characterising Nano Insulating Materials (NIM) And Infill Gases*, **Ofasa Abunumah**, P. Ogunlude, E. Gobina,* The Robert Gordon University, UK

Nano Insulating Materials (NIM) are useful materials for thermal control in systems, such as buildings and endothermic reactions processes. NIM possess nanopores that could contain rarefied gases that would aid or inhibit the insulation quality across thermal boundaries. The coupling of quantities interactions, such as the matrix's and gas's thermal conductivities, flow due to thermal (creep coefficient) and pressure gradients (bulk modulus), with NIM matrix micro and macro surface boundaries present design and manufacturing opportunities and challenges for NIM, instrumentations devices, and infill gas selection. Therefore, understanding these surface interactions occurring in vacuum or rarefaction gas dynamics is important to engineers and facilitates the effective design and application of NIM in domestic and industrial processes. Some authors have analytically investigated the insulating quality of NIM using rarefied gas flowrate, but none has investigated the opportunities of using gas mobility to characterize the insulating quality of NIM vis-à-vis low pressure and low-high thermal gradients. Hence the motivation for this study. Gas mobility is a combinatorial quantity that couples nanomaterial (permeability) and fluid (viscosity) properties, therefore making it an elite engineering quantity to potentially characterise NIM insulating quality. Thus, this work aims to provide a novel method for characterizing NIM systems using gas mobility.

Methodology and Materials:

An empirical approach involving gas experiments in nanoscale porous media was adopted for this study. Low pressures (0.20 – 1.00 atm), high temperature (up to 673K) were set as the working conditions. 5 analogous NIM core samples of varying structural parameters (macro surfaces-114, 118, 124, 300, and 524; pore size- 15nm, 200nm, and 6000nm; porosity-3%, 4%, 13%, 14%, and 20%; and aspect ratios- 4.5E-05, 8.0E-05, 1.6E-03, 1.9E-02, and 3.4E-02) and 4 common industry gases (CH_4, N_2, Air and CO_2) were the major materials used.

Experimental Results:

A total of 3,600 data points from 1,200 experimental were used for various analyses. The research was able to characterize NIM systems using gas mobility, industry criteria, such as Knudsen and Reynold's numbers, and gas laws, such as Boyles and Charles laws. Unlike flow rates, mobility responses to pressure and thermal gradients were very low. It was observed that gas thermal/insulating interactions with the micro and macro boundary surfaces of NIM, as measured by mobility, was heightened as pressure increases from 0.20 to 1 atm, this was further validated by the improved correlation values (R^2). CH_4 was found to be the most responsive to pressure and thermal boundary disturbances in NIM, while CO-$_2$ is the least. Therefore suggesting that a NIM filled with CO_2 gas offers better insulating quality than the other gases.

Contribution to Practice and Knowledge:

The multivariable (conditions, properties and parameters) settings to optimize mobility and the consequent optimal NIM system has been presented in detail. The merits and demerits of mobility-driven NIM analysis and decision making were highlighted. The outcome would find direct utility and practical application in NIM and instrumentation device manufacturing, and infill gas selection.

Keywords: Nano Insulating Materials, creep coefficient, mobility, bulk modulus, gas, nanotechnology

NS-Contributed On Demand-82 Realizing Gapped Surface States in the Magnetic Topological Insulator $MnBi_{2-x}Sb_xTe_4$*, **Wonhee Ko**,* Oak Ridge Natinal Laboratory*; M. Kolmer,* Ames Laboratory*; J. Yan, A. Pham, M. Fu,* Oak Ridge National Laboratory*; F. Luepke,* Forschungszentrum Jülich GmbH, Germany*; S. Okamoto, P. Ganesh, Z. Gai, A. Li,* Oak Ridge National Laboratory

$MnBi_2Te_4$ is one of the most promising candidates of intrinsic magnetic topological insulators (MTIs) that displays nontrivial band topology with an intrinsic antiferromagnetic state. However, there are inconsistent observations on the existence of the exchange gap of $MnBi_2Te_4$, partially due to the highly electron-doped nature of the $MnBi_2Te_4$ crystals and local inhomogeneity caused by the native defects. Here, we tailor the material through Sb substitution to shift the Fermi level into the bulk band gap and utilize scanning tunneling microscopy (STM) to assess the electronic structure and its local disorder. Quasiparticle interference and four-probe transport measurements displayed the surface states with a band gap of 50 meV for $MnBi_{1.36}Sb_{0.64}Te_4$ (MBST). The surface band gap is robust against the out-of-plane magnetic field despite the promotion of field-induced ferromagnetism detected by in situ magnetostriction measurement. However, atomic defects significantly affect the surface band gap by shifting the bands. The results indicate that further optimization of the defects in bulk-insulating MBST will offer a promising platform for exploring emergent topological phenomena. This research was performed at the Center for Nanophase Materials Sciences which is a DOE Office of Science User Facility.

NS-Contributed On Demand-85 Statistical Detection of Josephson, Andreev, and Single Quasiparticle Currents in Scanning Tunneling Microscopy*, **Wonhee Ko**, E. Dumitrescu, P. Maksymovych,* Oak Ridge National Laboratory

The tunnel junction between superconductors is the heart of many modern quantum information devices, such as superconducting qubits realized from quantum resonators with Josephson junctions. However, several tunneling mechanisms occur simultaneously in the superconducting tunnel junction, and thermal broadening further mixes them to obscure the identification of the tunneling mechanism. Here, we present a method to identify distinct tunneling modes in a tunable superconducting tunnel junction composed of superconducting tip and sample in a scanning tunneling microscope, specifically the one made of a Pb coated tip on a Pb single crystal. Combining the measurement of the relative decay constant of the tunneling current extracted from *I-V-z* spectroscopy with its statistical analysis over the atomic disorders in the sample surface, we identified the crossover of tunneling modes between single quasiparticle tunneling, multiple Andreev reflection, and Josephson tunneling with respect to the bias voltage even at a measurement temperature nearly half of the critical temperature. This method enables one to determine the particular tunneling regime independently of the spectral shapes, and to reveal the intrinsic modulation of Andreev reflection and Josephson current that is crucial for quantum device application of superconductors.

This research was performed at the Center for Nanophase Materials Sciences which is a DOE Office of Science User Facility.

NS-Contributed On Demand-88 Nanomaterial Adhesion Depends on Specific-Ion Effects Within Common Reservoir Fluids*, H. Chen,* Aramco Services Company - Boston*; S. Eichmann,* Aramco Services Company - Houston*; **Nancy Burnham**,* Worcester Polytechnic Institute

More efficient oil extraction would lower the need for environmentally risky infrastructure as well as lower the price of oil-based consumer products.Nanomaterials are used as tracers in oil-field characterization, for which minimal adhesion between the nano-tracers and rock (e.g. calcite) surfaces is desired.Building upon earlier experimental work, in which the tip of an atomic-force microscope (AFM) stood as a surrogate for a nano-tracer [1], we investigate the effects of i) ambient fluids typical of oil reservoirs and ii) surface defects using steered molecular dynamics simulations [2,3]. Media used to improve oil extraction include both fresh water and seawater.In our simulations, deionized water, salt-doped water ("seawater"), and calcium-doped seawater ("brine") were used as the fluids surrounding a carboxyl-terminated AFM tip above a defect-free calcite surface and also above both line and point defects on a calcite surface.As determined earlier [2], calcium ions preferentially bound to the calcite and carboxyl groups lowered the adhesion in calcium-doped fluids.Adhesion magnitudes of line and point defects were distinct in deionized water, with an average adhesion of (2.51 ± 0.78) nN. In comparison, in seawater the overall adhesion magnitudes remained similar to those of deionized water, (2.52 ± 0.75) nN, although their differences within seawater were generally no longer statistically significant. As for brine, the differences in adhesion among the defects were also generally no longer significant.However, the average adhesion magnitude of (1.27 ± 0.63) nN was markedly lower in brine than for the other two fluids.These results help understand nano-tracer sticking mechanisms and could improve the extraction of oil.

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**NS-Contributed On Demand-91 Walking the Plank: Solar Cell Nanowire Arrays Probed *in situ* by Surface Potential Microscopy*, Austin Irish*, *L. Hrachowina, R. Timm,* Lund University, Sweden

Nanostructured III-V semiconductors have brought third generation photovoltaic devices to the brink of mass application. InP nanowire arrays have already demonstrated excellent performance, offering high efficiency and low cost. Perfecting device fabrication and performance will require intimate knowledge and utmost control over the semiconductor nanosurfaces. We present an *in situ*,cross-sectional Kelvin probe AFM technique for measuring nanowires within the array along their axis. Whereas alternative methods involve destructively removing nanowires from their growth substrate, we keep the structures intact and on their original growth substrate. This ensures relevance and precision while probing *p-n* junction surfaces. Ambiently measuring arrays gives timely feedback for subsequent processing. Selectability allows comprehensive single-nanowires characterization when combined with other electronic/spectroscopic techniques (e.g. EBIC).

NS-Contributed On Demand-94 Probing Interfacial Properties of Iron Oxide Thin Films on Noble Metal Substrate by Scanning Tunneling Microscopy*, Dairong Liu*, *J. Schultz,* University of Illinois at Chicago*; S. Mahapatra,* University of Illinois at Chicago, India*; N. Jiang,* University of Illinois at Chicago, China

For the past several decades, scanning tunneling microscopy(STM) has enabled the atomic resolution study of the morphology and electronic characteristics of surfaces, including molecular adsorbates. However, the lack of chemical information critically limits its ability to fully define atomic environments. In contrast, optical spectroscopy is widely used to study the highly sensitive vibration fingerprints of chemical species. By combining STM with Raman spectroscopy, tip-enhanced Raman spectroscopy (TERS) can spectroscopically define interactions and chemistry at the spatial limit. This work highlights our investigations of subnanoscale surface structure. TERS enabled us to precisely probe molecule–molecule and molecule–substrate interactions at the nanoscale, such as distinguishing the packing model of subphthalocyanine (SubPc) on Ag(100) and discerning the localization of a subtle molecule–substrate interaction within the structure of a molecule. By pushing the spatial resolution below the level of nanoscale self-assembled molecular islands, TERS was found to offer the unambiguous characterization of molecular binding conformations and orientations that result in unique self-assemblies of rubrene with 5 Å spatial resolution. In order to address potential tip-related issues, we used Ar^+ ion sputtering of TERS probes, providing a method to recycle and preserve the plasmonic probes under UHV conditions, thus enabling their continued use for >2 months. This method further contributes to the implementation of TERS in different laboratories. In conclusion, these works develop TERS towards the study of highly localized inter-molecular interactions, which indicate the promising future of TERS in surface science research.

NS-Contributed On Demand-97 Room Temperature Spin Transport in Cd3As2*, Gregory Stephen*, *A. Hanbicki,* Laboratory for Physical Sciences*; T. Schumann,* University of California at Santa Barbara*; J. Robinson,* Naval Research Laboratory*; M. Goyal,* University of California at Santa Barbara*; S. Stemmer,* University of California Santa Barbara*; A. Friedman,* Laboratory for Physical Sciences

As the physical limits of CMOS loom closer, alternative state variable paradigms become increasingly important. Devices utilizing the electron spin as a state variable are especially promising due to their intrinsic non-volatility, speed, and versatility. Fully incorporating spintronic devices into next-generation computing systems requires optimized architectures and materials capable of efficiently harnessing the electron spin. One particularly promising class of materials are topological Dirac semimetals (TDS), exemplified by Cd_3As_2. TDS materials have high mobilities, 3D Dirac cones, and can exist in multiple quantum phases. We demonstrate the function of Cd_3As_2 as a channel for the flow of spin currents by incorporating it with hybrid graphene/MgO tunnel barriersas a non-local spin valve, the basic unit of spintronic devices for logic operations. We show that the spin valves operate at least up to room temperature.[1] We quantify the spintronic transport in the devices by measuring the spin Hall effect/inverse spin Hall effect, observing spin Hall angles up to $\theta_{SH} = 1.5$ and spin diffusion lengths of 10-40 μm. Long spin-coherence lengths with efficient charge-to-spin conversion rates and coherent spin transport up to room temperature, as we show here in Cd_3As_2, are enabling steps toward realizing practical spintronic-based computing systems.

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NS-Contributed On Demand-100 Reconstructing the Intrinsic Potential Energy Landscape of Interfacial Interactions With Thermally Modulated Force Spectroscopy*, Alan Liu*, *T. Sulchek,* Georgia Institute of Technology

Force probes are powerful experimental tools to measure the strength and physical extent of interfacial and intermolecular interactions at nanometer scales. However, because of the stochastic nature of force measurements, most force spectroscopy models require massive quantity of data in order to obtain meaningful energetic information of the interaction.We developed a force spectroscopy framework based on thermally modulated atomic force microscopy (AFM) force measurements capable of reconstructing energy landscapes of interfacial interactions over 100 nm distances from a handful of force curves. To address the challenge of insufficient sampling at the key points of the interactions, we defined exact equilibrium forces to serve as fiduciary markers that can be used to reliably overlay repeated force curves. The equilibrium force markers create a major advantage in that multiple under-sampled force measurements can be compiled as one fully sampled measurement of key regions of two state binding. We experimentally demonstrate the application of the method to find the intrinsic, continuous force and energy landscape reconstructed along an unprecedented 100 nm distance from merely 15 AFM force curves.

NS-Contributed On Demand-103 Open-Loop Amplitude-Modulation Kelvin Probe Force Microscopy Implemented in Single-Pass Peakforce Tapping Mode*, Gheorghe Stan*, *P. Namboodiri,* National Institute of Standards and Technology

Over many years, an abundance of developments and applications has made Kelvin probe force microscopy (KPFM) one of the most versatile nanoscale surface electronic characterization techniques. In the last years, significant developments were made to make KPFM faster, with direct measurement for the tip-sample contact potential difference (CPD), and free of feedback constrains. For example, the open-loop (OL) variants of KPFM provide access to the voltage response of the electrostatic interaction between a conductive AFM probe and the investigated sample. The measured response can be analyzed *a posteriori*, modeled, and interpreted to include various contributions from the probe geometry and imaged features of the sample. In contrast to this, the current implemented closed-loop (CL) variants of KPFM, either amplitude-modulation (AM) or frequency-modulation (FM), solely report on their final product in terms of the tip-sample contact potential difference. In ambient atmosphere, both CL AM-KPFM and CL FM-KPFM work at their best during the lift part of a two-pass scanning mode to avoid the direct contact with the surface of the sample. To address few of these impediments, we demonstrate here a new OL AM-KPFM mode implemented in the single-pass scan of the PeakForce Tapping (PFT) mode. The topographical and electrical components were combined in a single-pass by applying the electrical modulation in between the PFT tip-sample contacts, when the AFM probe separates from the sample. In this way, any contact and tunneling discharges are avoided and, yet, the location of the measured electrical tip-sample interaction is directly affixed to the topography rendered by the mechanical PFT modulation at each tap. Furthermore, because the detailed cantilever's response to the bias stimulation was recorded, it was possible to analyze and separate an average contribution of the cantilever to the determined local contact potential difference between the AFM probe and the sample imaged. The removal of this unwanted contribution greatly improved the accuracy of the AM-KPFM measurements to the level of the FM-KPFM counterpart.

NS-Contributed On Demand-106 Strain-modulated Electronic Properties in Epitaxial FeSn Thin Films on SrTiO$_3$(111)*, **Huimin Zhang**, Q. Zou,* West Virginia University, USA*; M. Weinert,* University of Wisconsin, Milwaukee,*; L. Li,* West Virginia University, USA

The crystal structure of FeSn consists of alternating Fe$_3$Sn Kagome and Sn honeycomb lattices, which provides a versatile platform for correlated topological phases hosting symmetry-protected electronic excitations and magnetic states. To date most work on FeSn was carried out on cleaved bulk materials.Here, we synthesize high quality FeSn thin films on SrTiO$_3$(111) substrates by molecular beam epitaxy. The growth mode is found to be 3-dimensional, and x-ray diffraction confirms single crystalline FeSn structure. Using low temperature scanning tunneling microscopy/spectroscopy, we observe perfect honeycomb lattice on the surface of the islands for film thickness above 10 nm, characteristic of Sn-termination. For film thickness less than 10 nm, periodic stripes due to distortion of the honeycomb lattice is observed, indicative of strain. On the deformed honeycomb lattice, we find enhanced local density of states at E = - 0.3 eV. We also observe various types of defects such as Fe anti-site and vacancy defects, which also modulate the electronic properties of FeSn.Our results demonstrate strain-controlled electronic properties in a Kagome magnet, key to developing its potential applications in future spintronic devices.

This research is supported by NSF (EFMA-1741673).

NS-Contributed On Demand-109 Structure-Function of PC Surfactants*, **Nir Kampf**, W. Lin, J. Klein,* Weizmann Institute of Science, Israel

Surfactants are surface-active materials that act as carriers and boundary lubricants.We compared the surface structure and function of three types of highly hydrated monomeric-, oligomeric- and di-block copolymer- based phosphocholine (PC) micelles.The AFM study under the surfactant solution showed that C$_{16}$PC and oligo-methacryloyl(dodecylphosphorylcholine) surfactants are organized in a worm-like micelles structure on the mica surface. On the other hand, di-block copolymer, poly(n-butyl methacrylate-b-2-methacryloyloxyethyl phosphorylcholine), PBMA-b-PMPC has a globular structure on the mica surface with a typical dimeter of about 20-40 nm. Friction measurements across the surfactants solutions using a Surface Force Balance technique demonstrate that monomeric or oligomeric surfactants show superior friction (friction coefficient, $\mu = 10^{-3}$), with higher robustness of the latter, up to at least 5 MPa. Due to its lower surface coverage, the PBMA-b-PMPC surfactants was less efficient as boundary lubricant. We conclude that multimeric PC-surfactants may provide highly-stable, robust micellar boundary layers with excellent lubrication properties in aqueous media to high contact stresses.

NS-Contributed On Demand-112 Selective Work Function Metal Etch Enabling Multi-Vt Patterning for High Performance Stacked Nanosheet Devices*, **Curtis Durfee**,* IBM Research*; S. Kal,* TEL*; M. Bhuiyan, S. Pancharatnam,* IBM Research*; M. Flaugh, I. Otto,* TEL*; H. Zhou, M. Belyansky,* IBM Research*; A. Mosden,* TEL*; N. Loubet, L. Meli,* IBM Research*; P. Biolsi,* TEL*; B. Haran,* IBM Research

Stacked gate-all-around nanosheet (GAA NS) device architecture provides the capability to co-integrate a wide range of channel width (W_{NS}), enabling simultaneous low-power and high-performance applications on a single chip [1-8]. This architecture creates the ability to fine tune V_t independently for nFET and pFET devices by using the work function metal (WFM) layers as sacrificial "patterning" layers. Furthermore, reducing the vertical space between the Si channels (T_{sus}) will provide additional improvement in the device performance [4,7]. However, T_{sus} scaling imposes significant integration and process challenges with High-K Metal Gate (HKMG) formation and WFM patterning [6, 7]; the traditional WFM wet etch solutions used for FinFET devices are insufficient to fully etch the pinched-off sacrificial layers between the Si channels for wide sheets (W_{NS}=100nm) due to the high aspect ratio [4], and to simultaneously stop on the desired layer for narrow sheets (W_{NS} = 20nm) due to low selectivity. This severely limits the etch options for WFM patterning in NS devices with wide sheets and scaled T_{sus}.

In this paper, we present a highly-selective dry etch process which completely etches sacrificial pFET WFM metal for wide nanosheets (W_{NS} = 100) from T_{sus} = 9 nm to extreme T_{sus} = 5nm (Fig. 1) without any damage to the underlying HK HfO$_2$ surface. Etch selectivity to HK and etch dependence with anneals on doped and undoped layers were characterized on blanket substrates. The dry etch process also was qualified on integrated structures using structural and electrical tests. We selectively removed pinched-off pFET WFM in the nFET regions and re-deposited the full nFET WFM stack around the HK material that envelopes the Si channel, as shown in Fig. 2. This technique enables multi-V_t patterning of nFET and pFET devices within the chip. M1 test results showed similar V_t, VBD, BTI at EOL and BTI slope for samples created with this technique and samples with "as-deposited" direct nFET WFM stack deposition (Fig. 3, 4). However, the wet etch process was self-limited; remaining pFET WFM prior to redeposition of the final nFET WFM caused degradation in V_t, VBD and BTI on wide sheets. There was no significant V_t degradation or variability across various W_{NS} from dry etch, indicating complete and selective etch of the pFET WFM.

We successfully demonstrated a gas phase WFM etch on stacked GAA NS devices. This novel isotropic and highly-selective etch capability is critical in facilitating WFM patterning, which enables multi-V_t tuning and further device performance improvement with T_{sus} reduction in high performance scaled NS logic devices [7,8].

NS-Contributed On Demand-115 Cooperative Effects in DNA Nanofabrication*, J. Majikes, P. Patrone, A. Kearsley,* National Institute of Standard and Technology*; M. Zwolak,* National Institute of Science and Technology*; **J. Alexander Liddle**,* National Institute of Standard and Technology

The Watson-Crick based pairing that enables sequence recognition and binding in DNA has been exploited in a variety of self-assembly schemes to build a diverse array of nanostructures.Although conceptually simple for single base pairs, the fabrication of DNA constructs can involve thousands of hybridization events, resulting in changes in enthalpy, entropy, and heat capacity that dictate the yield of the self-assembly process.The picture is further complicated by the fact that the energy scales relevant for DNA nanostructure assembly are on the order of kT at room temperature.This is essential for DNA's biological functionality but makes it difficult to engineer an assembly pathway to yield a target structure with high fidelity.We have worked to understand the self-assembly of DNA in the context of DNA origami, perhaps the most accessible and effective nucleic acid nanostructure fabrication methods [1].In a typical origami system, 200 staple strands (oligomers ≈ 30 bases long) hybridize with a long (≈ 7 000 bases) scaffold strand to form the completed structure.Each staple typically has three binding sites, each of which can exist in open, bound, or blocked states.An almost infinite number (3^{600}) of possible configurations may be explored during assembly.However, insight may be gained by examining what happens during a single staple-binding and strand-folding event.Using a novel affine transformation approach [2], we extract accurate and precise values of thermodynamic quantities from high-throughput fluorescent melt-curve experiments.Exploring a range of parameters, including staple strand concentration, change in scaffold strand topology on folding, and staple binding domain size, we quantify entropic effects [3] and identify a "blocked" state in which two related binding sites on the scaffold are each occupied by a staple, preventing a single staple from binding to both domains and creating a DNA origami fold.The blocked state becomes more likely for a single fold as the concentration of staple strands is increased.However, complete origami fold with high yield at high relative staple strand concentrations.This observation suggests that origami assembly is a result of a nucleation and growth process, following well-defined pathways in which each folding event strongly favors the occurrence of the next.We discuss our current understanding of cooperativity in self-assembly and its implications for nucleic acid nanostructure design.

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Nanoscale Science and Technology Division
Room On Demand - Session NS-Invited On Demand

Nanoscale Science and Technology Invited On Demand Session

NS-Invited On Demand-1 Engineering Quantum Forces and Torques*, Jeremy Munday,* University of California, Davis **INVITED**

The quantum vacuum gives rise to many effects that would not occur classically. One example is that the confinement of quantum electromagnetic fluctuations between two, isotropic macroscopic objects results in a force, i.e. the Casimir force. This force depends on both the geometry and the optical properties of the materials involved. An additional effect has been predicted for optically anisotropic materials, which can cause a rotation, i.e. a Casimir torque. Here we present our recent measurements of both of these phenomena. First, I will describe our results pertaining to the Casimir force between two spheres – a geometry that has previously eluded measurement due to experimental difficulties. Second, I will discuss additional geometries including pillars and holes that are now possible with this measurement technique and why they are interesting. Finally, I will conclude with a discussion of our recent measurement of the Casimir torque.

NS-Invited On Demand-13 Visualizing Inside of 3D Self-Organizing Systems by 3D-AFM*, Takeshi Fukuma,* Kanazawa University, Japan **INVITED**

Recently, three-dimensional atomic force microscopy (3D-AFM) has been proven to be a powerful tool for investigating various structures and phenomena at solid-liquid interfaces. In the method, a tip is scanned in the *XY* and *Z* directions in a 3D interfacial space. During the tip scan, the variations in the force applied to the tip is recorded to produce a 3D force image. At a solid-liquid interface, the tip interacts with surrounding solvent molecules during the tip scan. Thus, the obtained 3D image represents the distribution of solvent molecules. So far, the method has been used for visualizing 3D hydration structures on minerals, organic thin films, and biological systems with subnanometer-scale resolution. This emerging technology has attracted attention due to its potential applications in the research on interfacial control technologies for anti-fouling, lubrication, anti-freezing, colloidal dispersion, cosmetics and cleaning.

In the meanwhile, here I would like to draw attention to another important implication of the success of the 3D hydration measurements. In the AFM community, it has been a common sense that we should fix atoms or molecules to a solid surface to visualize them with atomic or molecular resolution. However, 3D-AFM allows us to visualize subnanometer-scale distribution of mobile water molecules that are not fixed on a solid surface. This is a big surprise and may lead to the breakthrough for the aforementioned limitation of AFM. Then, the next question would be what is the requirements to be visualized by 3D-AFM. We believe that the answer is capability of self-organization. For example, in the case of 3D hydration measurements, the hydration structure is significantly disturbed during the vertical tip scan yet it is quickly recovered before starting the next vertical scan. Such a self-organization capability is essential for visualizing inside of 3D structures. One may think this is too severe condition yet we can find large number of important 3D self-organizing systems in both natural and artificial environments. Examples include interfacial phenomena and devices (hydration, lubrication, electric double layer devices and liquid crystal devices) to biological systems (cells, nucleus, chromosomes and proteins). 3D-AFM may allow us to directly visualize inside of these various 3D self-organizing systems.

Based on this idea, we have recently started to explore inside of various 3D self-organizing systems: polymer-water interfaces, ionic liquid - electrode interfaces, and inside of chromosomes and live cells. With these examples, here I would like to propose to apply 3D-AFM not only for visualizing hydration structures but also for imaging inside of various 3D self-organizing systems.

NS-Invited On Demand-19 Tackling Instabilities in Hybrid Perovskites from the Macro- to the Nanoscale*, Marina Leite,* University of California at Davis **INVITED**

Halide perovskites for optoelectronics are often composed by micro- and nano-scale inhomogeneous constructs. Therefore, high spatial resolution characterization methods are required for mapping and quantifying their electrical behavior. In this talk I will present our latest developments on atomic force microscopy (AFM) methods to assess the dynamic physical and chemical processes that take once perovskite materials and photovoltaic devices are exposed to light. Briefly, we realize a 4D imaging method that enables mapping open-circuit voltage (Voc) changes with in real-time (16 seconds per scan), and at the nanoscale (< 50 nm in spatial resolution) based on illuminated Kelvin probe force microscopy (KPFM). Using this paradigm, we have demonstrated ion motion within a single nanoscale grain in $MAPbI_3$ solar cells upon 1-sun illumination, which results in a residual Voc that lasts for several minutes even under dark conditions. For multi-cation structures, we found that Cs-based perovskites deliver fully reversible and stable nanoscale voltage response, in excellent agreement with macroscopic measurements. We correlate the Voc nanoscale maps with chemical imaging through nano-IR and discover that the local variations in voltage are related to the power conversion efficiency enhancement in KI-treated perovskite. The heterogeneity revealed in both the local electrical and chemical responses reveals that the KI additive migrates our of the perovskite films, yet surprisingly; does not affect device performance. Our functional imaging platform can be extended to other perovskite materials, including Pb-free options. At the macroscopic scale, we provide a detailed comparison between $MAPbBr_3$ and $MAPbI_3$ through time-dependent voltage measurements. They reveal that, upon illumination, high-energy photons leads to a > 10x slower voltage decline toward equilibrium than low-energy photons in $MAPbBr_3$. Yet, $MAPbI_3$ shows wavelength-independent decay rate, resulting from ion migration. Through in situ photoluminescence (PL) under environmentally controlled conditions, we resolve a humidity-induced PL hysteresis. Further, we apply a machine learning algorithm to predict the luminescence response for > 12 hs. Concerning the unique behavior of multi-cation perovskites, a correlative microscopy approach is realized, combined with environmental-controlled PL measurements.

NS-Invited On Demand-31 Programming Assembly of 3D Nanoscale Systems*, Oleg Gang,* Columbia University **INVITED**

The ability to organize nano-components into the desired architectures with targeted properties can enable a broad range of nanotechnological applications, from energy materials to information processing. However, we are currently lacking an adaptable and broadly applicable methodology for the bottom-up fabrication of desired nanoscale structures. I will discuss our efforts on establishing a versatile assembly platform based on the molecular programming for guiding the formation of targeted architectures from nano-components of different types. The recent advances on assembly of targeted 2D and 3D periodic organizations, hierarchical structures, and arbitrary designed architectures from DNA-encoded abiotic and biological nano-components will be presented. Finally, I will discuss how these assembly approaches can be used for fabrication of nanomaterials with novel optical, mechanical, and catalytic functions.

NS-Invited On Demand-37 Nanoelectronic Devices and Architectures for Energy-Efficient Computing*, An Chen,* IBM Almaden Research Center **INVITED**

As the CMOS scaling driven by the Moore's Law approaching some fundamental limits, high power consumption and heat dissipation on chip have been recognized as the most critical challenges. The semiconductor industry has explored numerous nanoelectronic devices with the potential to achieve significantly lower power based on unconventional mechanisms, materials, and structures, including steep-slop transistors, phase-transition switches, spintronics, van der Waals devices, etc. For example, the Nanoelectronics Research Initiative (NRI) was funded by the Semiconductor Research Corporation (SRC) for over a decade to pursue the "next switch" beyond CMOS. Despite abundant scientific breakthroughs achieved in these device researches, no beyond-CMOS device has been demonstrated to significantly outperform CMOS for Boolean logic and von Neumann architectures. On the other hand, many nanoelectronic devices have shown unique characteristics, e.g., device-level reconfigurability, built-in memory-in-logic capability, tunable analog behaviors, programmable randomness, etc. They can be utilized in novel architectures and computing paradigms, including reconfigurable logic, analog and neuromorphic computing, compute-in-memory, nonvolatile logic, stochastic computing, etc.

To effectively utilize these unique characteristics in novel architectures, it is essential to cooptimize devices and architectures in order to achieve improved functionalities and efficiency. Both bottom-up (optimizing devices to meet architectural requirements) and top-down (designing circuit blocks and architectures to exploit device properties) approaches are needed. Sustainable and scalable technology advancement is often driven by material and device innovations; therefore, it is important to explore emerging materials and devices capable of native implementations of some novel computing paradigms. At the same time, CMOS technology has also been adopted in many novel computing paradigms, which presents not only a mature baseline for comparison but also a formidable competitor. Nanoelectronic devices and architectures need to provide convincing advantages in performance and efficiency over CMOS to justify significant research investment, which should be addressed by comprehensive benchmarking. A holistic approach from material exploration to device engineering and further up to architecture co-design has been emphasized in several research programs, including E2CDA (Energy-Efficient Computing from Devices to Architectures) at NSF, nCORE (nanoelectronic Computing Research) at SRC, etc. This presentation will discuss the opportunities and challenges of nanoelectronic devices and architectures for energy-efficient computing in the context of these recent research programs.

Undergraduate Poster Session
Room On Demand - Session OD-UP On Demand
Undergraduate Poster Session On Demand

OD-UP On Demand-1 Evaluating Hydrophobic Recovery of Nitrogen Plasma Treated Silk Fibroin Films*, **Chase Lenert-Mondou**, M. Hawker,* California State University, Fresno

Silk fibroin (referred to as silk) is a natural polymer derived from the cocoon of a silkworm. It has increased in popularity due to its potential uses in biomedical applications (i.e., tissue engineering, drug delivery, sutures, implants). However, the native silk polymer is hydrophobic, requiring modification to become more hydrophilic to promote cell adhesion and biocompatibility for in vivo applications. One of the techniques used to increase the hydrophilicity of polymers such as silk is low temperature plasma (LTP) modification. Nitrogen LTP has been well-documented as a strategy to enhance nitrogen-containing polar functional groups on a polymer's surface. LTP is a useful technique as it is a solvent-free, amenable process for polymer modification. However, LTP-modified polymers have been known to experience hydrophobic recovery, in which the surface reverts to a more hydrophobic state upon aging, making the hydrophilic modification short-lived. The hydrophobic recovery process has not previously been evaluated for silk using nitrogen LTP.

The goals of the present study were to 1) systematically explore the impact of varying key nitrogen LTP parameters (applied power and time) on silk film wettability, 2) study how the silk film secondary structure impacts the efficacy of nitrogen LTP modification, and 3) evaluate the hydrophobic recovery of silk films following nitrogen LTP treatment. Our initial water contact angle goniometry results demonstrated that varying plasma parameters had little effect on film wettability. To evaluate the potential impact of silk secondary structure on hydrophobic recovery, silk films were submerged in methanol for 30 minutes to induce beta sheet formation. This process drives water out of the matrix, causing the silk to adopt a more crystalline beta-sheet rich conformation. Methanol-treated silk films, along with unmodified controls, were then subjected to nitrogen LTP modification. Samples were aged under ambient conditions for up to 6 weeks, and film wettability was measured as a function of aging time using water contact angle goniometry to evaluate the hydrophobic recovery behavior. Methanol-treated and control silk films had initial water contact angles of ~60° and 70°, respectively. After nitrogen LTP treatment, silk films exhibited contact angles of ~23° and 35°, respectively, demonstrating a substantial increase in hydrophilicity. We will corroborate wettability data with FTIR, which was used to measure silk film secondary structure as a function of aging. We have observed minimal hydrophobic recovery after aging for 6 weeks, suggesting that nitrogen LTP can be used for long-lasting silk film modification.

OD-UP On Demand-4 Examining the Impact of BHT Inhibitor on the Microstructure of Spun-Cast Nanoporous Films of PMMA*, **Sadie Flagg**, T. Knippenberg, B. Augustine,* High Point University

Tetrahydrofuran (THF), a common organic solvent for polymers, is often stabilized with butylated hydroxytoluene (BHT) due to THF forming peroxide compounds. In prior work we have shown that solutions of 996 kg/mol poly(methyl methacrylate) (PMMA) dissolved at a concentration of 15.0 mg/mL in THF and spun-cast onto Si substrates produces thin nanoporous films unlike smooth films prepared from other solvents such as toluene and chloroform. In this study, we examined the effect of the interaction between BHT and THF on the PMMA films by varying the concentration of BHT present in the THF solutions from 0 - 5000 ppm. The influence of BHTs molecular structure was then examined by replacing the BHT with analogous compounds phenol and p-cresol in THF. Solutions also prepared with toluene and BHT were tested to determine if the films produced using BHT alone caused microstructural changes. Optical microscopy of the films exhibits color variation which may be due to opalescence caused by porosity variations in the films. All films were examined using tapping mode atomic force microscope (AFM) imaging. While the toluene/BHT and the THF/phenol solutions produced smooth non-porous films the p-cresol solution exhibited some areas of porous structure similar to the THF/BHT solutions. This suggests the importance of both the butyl and methyl groups in BHT in order to produce the nanoporous structure formation of PMMA. Varying concentrations of BHT appears to have a direct effect on the porosity of the films, although this may be dependent on the presence of water in the THF, as new anhydrous THF reproduced these results with less consistenly. We are in the process of performing molecular dynamic (MD) simulations on the solvent and inhibitor solutions to better determine the origin of the nanoporous film structure and thus understand the molecular interactions resulting in the film morphology.

OD-UP On Demand-7 Polymer Directed Synthesis of NiO/C for Supercapacitor Electrode*, **Manzili Kokayi**, B. Bastakoti,* North Carolina A&T State University

Supercapacitors are growing in popularity due to their cycling stability, quick charge-discharge rates, and high power density. These devices rely heavily upon the types of materials used within them. The capacitance of metal oxides can be higher than carbon based electrodes; however, they suffer from drawbacks such as low power density and poor conductivity. The present study explored the excellent design strategy for the synthesis of nanocomposites in which the pseudocapacitive NiO is intimately associated with a porous nanostructured carbon substrate. NiO was chosen because it has been shown to produce a synergistic effect when combined with carbon, creating a more stable electrode with higher conductivity. The use of polymeric templates in synthesis allows tuning the structure in nanoscale. The finding is very encouraging given easy synthetic routes and our material would be a very promising electrode material for future pseudocapacitors.

OD-UP On Demand-10 Insight Into the Formation, Desorption, and Structural Effects of Subsurface Oxygen on Ag(111) Using a Lattice-Gas Model and Monte Carlo Simulations*, **Elizabeth Lander**, C. Mize, L. Crosby, S. Roy,* University of Tennessee Knoxville

Theoretical gas-surface models are commonly utilized to compute elementary steps of surface chemistry. Adsorption, for example, is crucial in processes such as heterogeneous catalysis, chemical separations, protein denaturation, and nanoelectronics. To this end, we have developed a fully parametrizable lattice-gas model using electronic structure theory, which includes both surface and subsurface adsorption. Utilizing density functional theory (DFT), we have applied this model to investigate atomic oxygen adsorption on Ag(111). Our previous results on an unreconstructed surface show a high population of oxygen adsorbed in the second subsurface, the region between the second and third silver layers, at coverages in excess of 1/2 ML. Canonical Monte Carlo simulations indicate a similar distribution at temperatures of 600K, however, simulations of grand canonical Monte Carlo at 497 K and high oxygen pressure of 1020 Torr present little to no subsurface oxygen adsorption. In order to extend this model, we have introduced silver-silver and silver-oxygen pairwise interactions on and within the surface to allow for lattice distortion and reconstruction due to accumulation of atomic oxygen on the surface and in the subsurface. Through the addition of these interactions, our goal is to study the role of surface and subsurface oxygen in inducing well-known surface reconstructions of Ag(111), such as p(4x4) and c(4x8), as a function of surface temperature and oxygen pressure using Monte Carlo simulations.

OD-UP On Demand-13 Vapor Phase Synthesis and Characterization of Single and Few Layers of MoS2*, **Sabrina Jackson**,* NCA&T*; O. Ayanbajo, S. Shendokar, S. Aravamudhan,* NCA&T

Two-dimensional (2D) materials are excellent platforms to realize tunable quantum states. Among the many 2D materials, Transition Metal Dichalcogenides (TMDs) such as MoS2, MoSe2, WS2, and WSe2 are 2D Van der Waals materials with weakly bound atomic planes. For example, MoS2 (a TMD) is a lubricant and indirect bandgap semiconductor in its bulk form. However, when thinned down to a single layer form, it becomes a direct bandgap (1.9 eV) semiconductor with strongly bound excitonic and trionic states. Quantum computing could take advantage of this ability to control electronic and excitonic phase transitions in these atomically layered materials. In this work, we present a low temperature synthesis process to produce high quality single and few layers of MoS2 using direct vapor phase sulfurization of MoO3. Characterization were performed by Raman Spectroscopy, Atomic Force Microscope, and Electron Microscopy techniques.

OD-UP On Demand-16 Characterization of Ru-ZrO$_2$ Water Splitting Catalyst*, Paul Bean, P. Godbold, S. Zhang,* University of Virginia

Much research into nanoparticle synthesis is motivated by the desire to control catalysis. Nanoparticle size, composition, and architecture are major contributors to catalytic activity and stability. Thus, it is of interest to develop well-defined nanostructures in order to precisely control activity and increase stability. In the Zhang lab at UVA, we are developing methods to form active single atomic sites in metal oxides. A variety of characterization methods – namely Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM), and Energy Dispersive x-ray Spectroscopy (EDS) – allow us to characterize the synthesized nanomaterials. Use of these two microscopy techniques in tandem reveal the morphology of our material on a scale from multi-microns to several nanometers, while EDS can analyze the elemental composition of our metal. Following our lab's recent development of well-defined single site Co doped TiO2 nanorods, which are highly active and stable in alkaline oxygen evolution reaction (OER), we are investigating the synthesis of single site Ru doped ZrO2 for use in acidic OER. Initial electrochemical testing has shown Ru-ZrO2 to be both active and stable in acidic conditions, making this an ideal candidate for optimization. TEM imaging show that most methods yield similar nanoparticles, but co-inspection with SEM and EDS reveals an uneven Ru distribution in some synthesis, suggesting that certain precursors and amounts of Ru encourage the formation of separate Ru-dominate oxides as opposed to forming evenly doped Ru-ZrO2 particles.

OD-UP On Demand-19 Extreme Atomic-Scale Surface Roughening: Amino Acids on Ag on Au(111)*, **Emily Cook**, K. Boyd, J. Phillips, M. Paszkowiak, E. Iski,* University of Tulsa

Electrochemical scanning tunneling microscopy (EC-STM) has unique benefits over the more commonly used ultrahigh vacuum STM (UHV-STM). EC-STM has the ability to perform electrochemical techniques such as cyclic voltammetry (CV) and imaging while applying a potential to the surface in ambient conditions and under a liquid layer. This allows for surface studies to be extended to biologically relevant conditions to further understand biomolecule-surface interactions. As technology continues to decrease in size, altering metal surfaces on the nanoscale using biological molecules is advantageous because biomolecules are ubiquitous and non-toxic. Furthermore, metal surfaces can act as a substrate on which amino acid self-assembly can be studied to better understand the origins of homochirality.

Thin films are a form of surface modification where a small amount of material is deposited on a surface and due to its thinness, the film can have different properties than its corresponding bulk material. An example of this is a Ag monolayer deposited via underpotential deposition (UPD) on Au(111) which was found to be thermally stable up to 1,000 K. However, this property only held when the Ag was deposited in one of two UPD potential regions. Moreover, studies of amino acids on Au(111) demonstrated that the amino acids can trap Au adatoms into single atom high islands on the surface, with the island areas increasing as a function of amino acid molecular weight. As the surface temperature was increased, the island areas grew in area and height, demonstrating a Volmer-Weber (VW) growth mode.

To further understand the chemical properties of Ag thin films, L-isoleucine was added on a Ag monolayer on Au(111). This resulted in a markedly different surface morphology than a Ag monolayer on Au(111) or amino acids on bare Au(111) because there was the observation of extreme surface roughening that encompassed many layers of the surface, with each layer having the height of one Au or Ag atom. It is hypothesized that the carboxyl and amino groups of the molecule chelate the metal atoms and remove them into solution or move them across the surface to promote roughening. The Ag thin film changes the surface energy to result in an alternative and unexpected growth mode that involves growth out of and into the surface and provides a mild, electrochemical method by which surface roughening can occur.

OD-UP On Demand-22 Examining Internal Temperatures of Nitrogen-Containing Plasmas to Understand the Gas-Catalyst Interface*, **Melanie Fouts**, J. Blechle,* Wilkes University

In an effort to address growing environmental concerns, selective reduction of nitrogen oxide pollutant gases (N_xO_y) generated from vehicular and industrial exhaust is of increasing importance. Currently, the three-way catalytic converter serves as the primary method of pollution control, however such systems suffer from reduced efficacy at lower temperatures and are hindered by an inability to chemically reduce all relevant nitrogen oxides. One promising alternative is plasma-assisted catalysis (PAC) which can improve energy-efficiency and reaction selectivity at preferred operating conditions. Despite these advantages, such systems have yet to see commercial use due to the complexity of the plasma's extensive parameter space. Thus, there is a need to understand the influence of plasma conditions on the chemistry at the gas-surface interface.

To this end, a model PAC system was designed by interfacing inductively coupled plasmas with catalytic substrates. Specifically, plasmas formed from N_2 and O_2 feed gases were studied in the presence of ceramic, precious metal, and composite catalysts. Optical emission spectroscopy (OES) was used to determine internal temperatures and densities of N_2 and NO molecules based upon changes in applied power (25–200 W), system pressure (50–200 mTorr), and the method of substrate implementation. In 100 mTorr N_2 plasmas, calculated vibrational temperatures (T_v) for N_2^* ($C^3\Pi \rightarrow B^3\Pi$) increase proportionally with a linear dependence on applied power (4400-6000 K). By contrast, the addition of a ceramic material both individually and as a composite ceramic-Ag surface results in a ~12% drop in T_v across all powers (3500–5000 K). However, the Ag substrate alone does not influence T_v, except at 200 W when values decrease by ~10% relative to the pure N_2 plasma (5400 K). Diagnostic OES data collected across all system conditions will also be correlated with SEM analysis to examine changes in surface morphology. This comparison allows for improved understanding of the interconnected relationship between reactive species and catalytic surfaces. Such measurements provide insight into the complex energetic environment of the plasma and are crucial to unraveling the mechanisms that will lead to future PAC success.

OD-UP On Demand-25 Oxygen-Induced Surface Reconstructions on curved-Ag(111)*, **Faith Lewis**, D. Killelea,* Loyola University Chicago

Curved crystals allow for systematic investigation of the roles of terrace widths and geometries in surface reactions. We seek to understand how the (111) terrace width affects the growth and morphology of oxygen-induced surface reconstructions on Ag(111). Scanning tunneling microscopy (STM) was used to obtain atomic scale images of oxidized c-Ag(111) surfaces to determine what phases were present after various exposures to gas-phase atomic oxygen (AO). My project specifically looked at absorption patterns, in particular the low-temperature striped phase and the *p*(4x5√3)-O adlayer, and under what conditions and step widths they were favored.

OD-UP On Demand-28 Water Adsorption on Curved Ag Surfaces*, **Christina Grytsyshyn**, D. Killelea,* Loyola University Chicago

Studies of water adsorption on metal surfaces provides insight to the nature of water-water and water-metal interactions. Observing the adsorption of D2O on a curved Ag(111) crystal will allow for the investigation of how water interacts with the different facets of the surface, where the molecules will be arranged differently, thus allowing data to be gathered on water's interactions with multiple surfaces all in the same experiment. The surface interactions and adsorption locations will be studied using a combination of temperature programmed desorption (TPD) and scanning tunneling microscopy (STM) experiments. The water structures formed display the balance of attractive and repulsive forces, and how water molecules arrange themselves on the surface of a metal can give insight on the catalytic properties of that metal, providing necessary fundamental information for further research.

OD-UP On Demand-31 Crystal Growth and Magnetic Properties of MgCr$_2$O$_4$*, **Ajeya Dixon**, S. Karna, D. Temple,* Norfolk State University

Spinels containing transition metals or rare earth elements have been extensively studied as prime candidates to exhibit geometric magnetic frustration. Chromium-rich spinels, such as $ZnCr_2O_4$ and MgCr2O4, have attracted particular attention due to antiferromagnetic ordering transitions at low temperature that are coupled to lattice distortions. Recently, we have grown $MgCr_2O_4$ single crystal using floating zone crystal growth technique and will perform structural and magnetic characterizations in near future. X-ray powder diffraction refinement indicates that the crystal structure is cubic having Fd-3m symmetry.

OD-UP On Demand-34 Single Crystal Growth of Bi2CuO4 Using the Optical Floating Zone Technique*, **Tekiyah Robinson**, S. Karna, D. Temple,* Norfolk State University

Topological materials having 8-fold electronic degeneracy protection by nonsymmorphic symmetries of a crystal exhibit double Dirac fermions which have been predicted in $CuBi_2O_4$. In addition, more recent and accurate density functional theory calculations demonstrate that it should be an antiferromagnetic Mott insulator. Here, we have grown $CuBi_2O_4$ single crystal using floating zone crystal growth technique. First, polycrystalline $CuBi_2O_4$was synthesized by the direct solid-state reaction of Bi_2O_3 and CuO ina 1:1 molar ratio, mixed thoroughly using a mortar and pestle. X-ray diffraction was employed to check phase purity of the polycrystalline samples and confirmed that $CuBi_2O_4$ crystallizes in the space group *P*4/*ncc* which consists of planar $[CuO_4]^{6-}$units with Bi^{3+} ions occupying the spaces between units. The resistivity and magnetoresistance measurements are planned to do in near future on $CuBi_2O_4$ single crystal.

OD-UP On Demand-37 Characterization of Triple Cation, Mixed Halide Perovskites in Deposited in Near-Ambient Conditions*, **Samuel Candelario Torres**,* North Carolina Central University*; N. Edwards,* North Carolina Central Univesity*; M. Wu,* North Carolina Central University

Lead halide perovskites combining Cs, formamidinium and methylammonium cations with iodine and bromine anions demonstrate increased stability compared to single cation perovskites and photovoltaic conversion efficiencies exceeding 20%. These perovskites are sensitive to moisture during thin film deposition, with most reported films fabricated in nitrogen filled gloveboxes, and rapidly degrade under exposure to high relative humidities. The addition of lead thiocyanate has recently been shown to increase film quality and improve moisture tolerance. We report here on the fabrication of triple cation mixed halide perovskites in a 10% relative humidity environment, investigating the impact of the addition of lead thiocyanate on film morphology and the lifetimes and diffusion coefficients of photogenerated charge carriers. From confocal photoluminescence (PL) microscopy, we conclude that the addition of lead thiocyanate at concentrations of 2 - 8 wt% increases grain sizes and reduces compositional heterogeneity over micron length scales. Time resolved photoluminescence mapping measurements confirm this increased film quality, with increased carrier lifetimes and reduced lifetime dispersion observed in samples with lead thiocyanate. Diffusion coefficients determined through time resolved photoluminescence microscopy with spatially fixed excitation and spatially scanned collection showed reduced diffusion coefficients, but increased diffusion lengths after the addition of lead thiocyanate. These findings provide guidance for potential low-cost fabrication of perovskite solar cells.

Plasma Science and Technology Division
Room On Demand - Session PS-Contributed On Demand

Plasma Science and Technology Contributed On Demand Session

PS-Contributed On Demand-1 Forming Protection Layers Using $SiCl_4$ Plasma for Highly Selective Etching*, **Miyako Matsui**,* Hitachi Ltd., Japan*; K. Kuwahara,* Hitachi High-Tech Corp., Japan

Three-dimensional patterning for fabricating fin-based field-effect transistors (Fin-FET) has increasingly necessitated etching processes with a higher selectivity in three dimensional and fine-pattern structures. Highly selective etching techniques require advanced processes to form protective layers on unetched materials, such as masks, sidewalls, and etch-stop materials.

In this study, we investigated a deposition process for forming protective layers on top of masks by using $SiCl_4$ plasma generated by a microwave-ECR etching system. This process is effective for achieving extremely highly selective etching by depositing protective layers on unetched materials in the etching chamber before the etching procedure. In our experiments, a protective layer was formed only on the top of a line-and-space pattern as a mask before the bottoms of the line-and-space patterns were etched.

We suggested a process for forming uniform protective layers on the top of a pattern by using a deposition step followed by a uniformization step. During the deposition step, $SiCl_4/CO_2$ plasma was used to form a SiO_x protective layer only on the top of the pattern. Duty cycle of the pulsed microwave affected the cross-sectional profile of the protective layer by controlling the plasma dissociation. During the re-etching step, the protective layer was re-etched using NF_3/Ar plasma to clean the deposited layers formed at the bottoms of the pattern and improve the thickness distribution on the top of the patten within the wafer. The cross-sectional profile of the protective layer formed on the top of the pattern was also improved to the one desired by the re-etching step. According to XPS analysis of the protective layer, we found that etching rate of the protective layer during the re-etching step depended on the atomic concentration of C contained in the protective layer. This was because the C atoms contained in the SiO_x protective layer caused a SiO_x etching reaction by forming CO and SiF_x.

We also developed a cyclic process, in which deposition and re-etching were carried out alternatively to etch the bottoms of the pattern using the protective layer as a mask. Using the cyclic process to form a SiO_x protective layer on a line-and-space sample, we demonstrated that the uniform etching of SiO_2 layer formed at the bottom of the patterns without etching over the top of the original pattern.

PS-Contributed On Demand-4 Focus Ring Erosion During Plasma Etching: Consequences of Dielectric Constant**, **Xifeng Wang**,* University of Michigan*; H. Lee, S. Shim, S. Nam,* Samsung Electronics Ltd., Korea (Republic of)*; M. Kushner,* University of Michigan

In plasma etching reactors, the structure surrounding the wafer, the a focus ring (FR), plays an important role in maintaining uniform fluxes of reactants across the wafer. The FR is typically made of dielectric materials. During etching, the sheath that forms over the wafer to accelerate ions into the wafer extends over the FR. Electrical charging of the FR modifies the sheath relative to that over the wafer. One wants the sheath uniform across the wafer-FR boundary to maintain etched critical dimensions (CDs) to the edge of the wafer. On the other hand, maintaining a high voltage sheath over the FR will erode the FR. A compromise is often made to maintain uniform fluxes and ion energy and angular distributions (IEADs) to the edge of the wafer while not significantly eroding the FR.

In this work, we computationally investigated the consequences of dielectric constant ε of the FR materials on FR erosion and uniformity of fluxes to the wafer. Reactor scale modeling was performed using the Hybrid Plasma Equipment Model (HPEM). The etching of the wafer and erosion of the FR was simulated by the Monte Carlo Feature Profile Model (MCFPM). A dual-frequency capacitively coupled plasma reactor was used with a 60 MHz high frequency (HF) source applied to the top electrode and a 5 MHz low frequency (LF) bias applied to the bottom electrode. The powers of the HF and LF in the base case were 600 W and 1000 W. The gas mixture was $Ar/C_4F_8/O_2$ at a flow rate of 600 sccm and pressure of 30 mTorr. The top surface of the FR was quartz.

The series capacitance of the FR and its underlying structure is typically smaller than that of the wafer and its underlying structure. As a result, the FR charges quickly during the radio frequency cycle, which reduces the voltage drop across the sheath on top of the FR. The IEADs striking the FR are therefore generally lower energy with broader angular distributions. At the transition between the wafer and the FR, there is an angular skew in the IEADs that results from the difference in sheath thickness above the wafer and the FR. This skew, as well as the erosion rate across the FR, are functions of the dielectric constant of the FR base material. With low ε, the FR charges quickly, less plasma is produced above the FR and there is less voltage across the sheath which results in less FR erosion. Increasing ε of the FR produces a higher sheath voltage as well as higher ion fluxes over the FR which increases erosion, while the skew at the edge of the wafer is less severe.

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PS-Contributed On Demand-7 Improving Estimation Accuracy of Film Thickness Using Machine Learning for End Point Detection in Dry Etching*, T. Okamoto, **Soichiro Eto**,* Hitachi Ltd., Japan*; S. Nakamoto, K. Fukuchi, R. Asakura,* Hitachi High-Tech Corp., Japan

Precise control of fabrication in each process is required in semiconductor manufacturing because the device structure is now three-dimensional and miniaturized. In a dry etching process, an end point detection (EPD) system that adjusts the etching time for each process is widely used to suppress the variation in the etched film thickness between wafers. In this system, the film thickness of the etching-target material is estimated based on the light spectrum reflected from a wafer during etching, and the etching process is stopped when the estimated thickness reaches a target value.

The accuracy of the film thickness estimation using EPD decreases when the wafer structure, such as the mask or sublayer film, differs for each wafer. For example, in an etching process after forming an etching mask, wafer-to-wafer variation in the mask thickness could occur. In this case, even though the film thickness of the etching-target material is the same, the accuracy of the film thickness estimation using EPD decreases because the light spectrum of the wafer has a different shape depending on the mask thickness. Therefore, high robustness against the variation in the device structure is required to estimate the film thickness accurately.

This study proposes a new method of film thickness estimation using a regression model of the relationship between the light spectrum and film thickness. A regression model based on the light spectra of wafers was created using machine learning to estimate the film thickness of wafers with various device structures precisely. Kernel ridge regression, which can create a nonlinear regression model, was used as the algorithm because the light spectrum changes nonlinearly with film thickness.

The accuracy of the film thickness estimation using the regression model for the wafers with various device structures using simulated light spectrum was examined. The light spectrum of the wafers in the Si_3N_4 film etching process was generated using an optical simulation, and the thickness of the SiO_2 mask on the Si_3N_4 film was changed as a parameter of the variation in the device structure. The model was created based on the calculated light spectra of the wafers with various mask thickness. Then, the Si_3N_4 film thickness of the wafers with each mask thickness was estimated using the regression model. As a result, the Si_3N_4 film thickness of the wafers could be estimated with an error of 1 nm or less. High accuracy was possible in the film thickness estimation for the wafers with mask thickness that the regression model had not learned. Therefore, our proposed method has high robustness against variation in the device structure.

PS-Contributed On Demand-10 Floating Wire Assisted Plasma With Vapor Injection of Liquid Mixtures for Etching Titanium Compounds*, 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

Advanced fabrication of three-dimensional (3D) devices in semiconductor industry required to control isotropic etching of multiple metal gates made of titanium containing compounds. A wet etching of the Ti compounds is conventionally used with H_2O_2 mixtures; however, there are only few reports for success of wet etching of these compounds. In this study, we have been developing a new dry etching method, called atmospheric pressure plasma enhanced atomic layer etching (APP-ALE) for isotropic etching of the Ti compounds by using a floating wire-assisted atmospheric pressure (FW-APP) with vapor injection of liquid sources.

In surface modification processes, fluxes and energies of ions, radicals, electronically excited particles, and photons in the visible and UV range should be controlled. Here radicals are more stable and are able to travel long distances in flowing gases or by diffusion in our setup. The FW-APP source consists of a 200-mm-high discharge quartz tube with a three-turn Cu coil connected with a VHF power of 100 MHz and a long floating metal wire placed inside to improve the plasma generation at a remote region.[1,2] The FW-APP has a high electron density (10^{14} cm^{-3}), and a high radical density is produced. Vapors generated from liquid sources were injected into the plasma contact region on the sample surface for surface modifications of the Ti compound film. Radicals were detected from optical emission spectra of the plasma. Surface modification of the Ti compound surface was analyzed by X-ray photoelectron spectroscopy.

In a similar manner of the atomic layer etching, the modified layer with lower surface binding energy can be removed by an additional step. The reaction chemistry of FW-APP at sample surface brings a large difference in chemical kinetics as compared with low pressure plasma. Rich radical source that can work as a co-reactant or etchant species enhances the reaction rate with the sample surface. Therefore, APP-ALE seeds the prospect of developing a high-performance etching method with low-cost, large-area, and high-speed treatment at relatively low substrate temperatures.

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PS-Contributed On Demand-13 Plasma Based ASD for EUV Resist Defectivity Reduction and Process Window Improvement*, Jennifer Church,* IBM Research Division, Albany, NY*; K. Lutker-Lee,* TEL Technology Center, America, LLC*; L. Meli, E. Miller,* IBM Research Division, Albany, NY*; A. Raley,* TEL Technology Center, America, LLC

EUV lithography has overcome significant challenges to become an essential enabler to the logic scaling roadmap [1]. However, it remains limited by stochastically driven defects, such as line breaks and line bridges for aggressive pitches. [2] This is especially relevant for the back end of line (BEOL) which requires the most aggressive scaling [3]. Stochastic defects reduce device yield and may push device manufacturers to move to EUV multi-patterning beyond 36nm pitch single exposure which is a costly option.

While the lithography and patterning stack can be optimized to provide the largest process window with the lowest number of defects, process margins decrease as smaller pitches are required [2]. Currently, for some lithography stacks, especially spin on glass (SOG) based tri-layer stacks, the defect free process window beyond 36nm pitch is limited by line collapse [4]. Reduction in resist thickness may mitigate pattern collapse, but it may also increase the number of line breaks – trading one killer defect for another [5].

In this presentation we expand on an area selective deposition (ASD) process in-situ of an etch chamber to selectivity deposit material on the EUV photoresist prior to transferring the pattern downstream.[6,7] We demonstrate mitigation of resist line notching and breaks while maintaining deposition free open areas and clear alignment marks. Due to the inherent chemical selectivity of the deposition process as opposed to a purely aspect ratio driven deposition process, thinner resists that, with a normal etch condition would results in line breaks, can now be considered. This drives down flop-over defect issues seen with thicker EUV resists and enables several underlayers systems that could otherwise not be considered. Finally we demonstrate that defectivity levels measured by e-beam inspection post lithography and post pattern transfer and yield are both improved at 30nm pitch when this ASD process is used.

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PS-Contributed On Demand-16 Extreme Contact Hole Shrink for BEOL Connectivity*, **Filip Schleicher**, S. Paolillo, S. Decoster, C. Wu, V. Vega Gonzalez, F. Lazzarino,* IMEC, Belgium

Extreme scaling of dimensions in the semiconductor industry requires not only novel materials but also advanced patterning concepts. One of such challenges is the Back End Of Line (BEOL) interconnect via etch which requires increasingly higher aspect ratios and lower bottom Critical Dimensions (CD) with tight control in order to ensure proper landing on the metal line below. In this paper, several etch approaches to pattern a via landing on Metal Pitch (MP) 21nm will be shown. Etch chemistry has been fine-tuned at several steps in attempt to adjust shrink at different levels of the stack while still maintaining vias open. Moreover, liner-assisted shrinkage, both organic and inorganic, have been implemented. As a result, BEOL vias of aspect ratio of 10 and the bottom CD of 10.5nm have been achieved. Low CD Uniformity (CDU), Local CDU (LCDU) and defectivity have been identified by numerical analysis, large area Voltage Contrast (VC) technique and Transmission Electron Microscopy (TEM), showing correct landing of vias on the metal below. Results point to several etch shrink options for scaled BEOL vias, which can be implemented in the industry-grade interconnects.

PS-Contributed On Demand-19 Direct Metal Etch of Molybdenum and Ruthenium: Patterning Challenges for N3 and Beyond*, Stefan Decoster****, S. Kundu, F. Lazzarino,* IMEC, Belgium*; E. Camerotto,* LAM Research, Belgium

For several decades, the semiconductor industry has been successfully following Moore's law. This has been achieved by a combination of dimensional scaling, introducing new patterning concepts, innovative device architectures, design-technology co-optimization, tool improvements, and integrating new materials. In the back end of line (BEOL), the Al-based interconnects were eventually replaced in the mid 90's by Cu-based interconnects. However, in contrast to Al or Al-alloys, direct metal etch of Cu turned out to be too challenging. Therefore, the direct metal etch approach was replaced with damascene patterning, i.e., defining trenches and vias in a dielectric material and then filling these structures with a metal, such as Cu.

Although damascene patterning has many technical challenges, Cu-based interconnects have been around for almost three decades in many consecutive technology nodes. As we are slowly progressing towards metal pitches of 20 nm and smaller in the BEOL interconnects, the resistance of Cu metal lines is increasing rapidly due to surface and grain boundary scattering. Therefore, many research efforts are currently spent to find alternative metals to replace Cu at these small pitches, both for metal lines as well as for vias. Two interesting candidates, which are expected to have a so-called cross-over point with Cu at very small dimensions (~10nm) are Ruthenium (Ru) and Molybdenum (Mo).

An important advantage for Ru and Mo is that both materials can be patterned through direct metal etch, which simplifies the overall patterning flow, and eventually opens up the possibility for exploring new integration concepts and patterning approaches. During the last few years, we have investigated at imec the direct metal etch of both materials, starting at a more relaxed metal pitch of 32 nm, but targeting to scale down towards 18 nm metal pitch.

In this work, we will not only share the status of the direct metal etch of Ru and Mo at imec, but also focus on the challenges that arise when patterning these metals at such small pitches. While Ru patterning is being impacted by oxidation of the hard mask, the major challenges for Mo patterning are the sidewall protection and the oxidation of the metal lines. Finally, we will share the results of the efforts to mitigate these obstacles.

PS-Contributed On Demand-22 High Aspect Ratio Supervia Dual Damascene Etch for iN5 and Beyond*, Harinarayanan Puliyalil,* IMEC, Leuven, Belgium*; Y. Feurprier, N. Oikawa,* Tokyo Electron Miyagi Ltd., Japan*; V. Vega Gonzalez, B. Briggs, D. Montero, F. Lazzarino, Z. Tokei,* IMEC, Leuven, Belgium*; S. Nakamura, S. Tahara, K. Kumar,* Tokyo Electron Miyagi Ltd., Japan

Challenges in the BEOL CMOS scaling towards advanced technology nodes are mainly due to the limitations coming from routing congestion and RC delay [1]. One of the ways to address these scaling challenges for technology nodes beyond iN7 is to implement scaling boosters such as High Aspect Ratio (HAR) supervia. Supervia can be defined as a high aspect ratio via that connects two metal layers by-passing the contact with the intermediate metal layer, while the supervia will be self-aligned to the trench hard mask. Benefits of supervia over conventional 'stacked' single level vias is reported elsewhere [2].

Primary challenge in supervia patterning includes etching through multi-layer dielectric stack without damaging the limited thickness of available trench hard mask. Continuous plasma exposure to the trench hard mask at the via location may induce corner erosion due to combined effect of radical induced chemical etching and ion induced sputtering. Any such potential damage to the trench hard mask will cause loss of via self-alignment and potential shorts with the neighboring lines. This challenge could be addressed to certain extent by increasing the polymer deposition rate on top of the hard mask during the via etch process, which could act as a potential protective layer to prevent HM erosion. However, this increases the risk of via etch stop, predominantly noticed in isolated structures due to dense-iso etch loading. Furthermore, controlling the via CD and profile while patterning through multi-layer stack at a high aspect ratio (AR >10) is another challenge.

This abstract presents demonstration of 2-level supervia using an EUV via mask to connect metal layers M3- M1 on a BEOL iN5 test vehicle (M3 metal pitch 32nm). Challenges in supervia patterning such as density-dependent etch, CD-dependent etch, maintaining the self-alignment, controlling the via CD and via profile are addressed. Finally, 3-level supervia DD etch process enabling connection between M4 & M1 is demonstrated in an exploratory etch chamber (TEL) which enables supervia with better control over via self-alignment, CD and profile control.

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PS-Contributed On Demand-25 Impacts of Different Carrier Wafers during Cl_2 Inductively Coupled Plasma Etching on the GaN Surface and the Al_2O_3/Gan Interface*, Thibaut Meyer****, S. Boubenia, C. Petit-Etienne, B. Salem, E. Pargon,* CNRS-LTM, Université Grenoble Alpes, France

In several decades, the semiconductor industry has witnessed drastic structural changes due to the growing electric power consumption. To satisfy the future requirements, alternative semiconductors are currently investigated to outperform the electrical performances of silicon-based devices. Among those materials, Gallium nitride (GaN) can sustain high voltage and high current in extreme condition, making it an adequate semiconductor for high power electronics.Several approaches have been proposed to develop GaN Metal-Insulator-Conductor High-Electron-Mobility Transistors (MIS-HEMT). In the MIS-HEMT structure, the dielectric/semiconductor interface is a key issue to improve the MIS-HEMT performances. It is known that the semiconductor surface is deteriorated during the etching step. The main guideline is to achieve a damage-free surface and, in this way, to reduce the interface trap density. In typical industrial processes, the mask coverage is such that undesired species (Si, C, O, H) are inevitably introduced in the plasma. Nevertheless, their influences on the plasma properties, the GaN surface and ultimately the Al_2O_3/GaN interface are not fully addressed.

In the present study, the presence of a mask is simulated by fixing GaN samples on 300 mm wafers (photoresist, thermal SiO_2 and LPCVD Si_3N_4) in an Cl_2 Inductively Coupled Plasma. The bias potential was varied from the plasma potential (V_p) to - 200 V, whereas the other plasma parameters were kept unchanged. All investigated carrier wafers react differently, exhibiting significant differences of the etch rates (Fig 1a). The chlorine atoms consumption and the redeposit of etch byproducts affect significantly the GaN etch rate (Fig. 1b), the surface morphology (Fig. 1c) and the surface composition. It is in that context that excited species (Cl, $SiCl_x$, C_2, H, CCl, N_2) were monitored by Optical Emission Spectroscopy (Fig 2). Atomic Force Microscopy was performed after Cl_2 etching to evaluate the modification of the surface morphology. *In situ* X-ray Photoelectron Spectroscopy was implemented to probe the surface composition after the etching (Fig. 3) and after the atomic layer deposited Al_2O_3. The Al_2O_3 layer was inserted between a gate metal (Au/Ni) and the etched GaN in order to perform C-V measurements.

When using a SiO_2 carrier wafer, a rough surface is associated with the presence of SiO_x nonvolatile etch products on the GaN surface. Overall, we note a similar smooth surface with Si, photoresist and Si_3N_4 carrier wafers. The N/Ga ratio is almost not degraded except with a Si carrier wafer, which induces a strong Ga-depletion regardless of the bias potential. C-V measurements are ongoing to evaluate the impact of the bias and the carrier wafer on the electrical performances of the etched GaN.

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PS-Contributed On Demand-28 Wireless Retarding Field Analyzer for Ion Energy Distribution Measurements in Plasma Processes*, David Gahan,* Impedans Ltd, Ireland

Planar retarding field analyzers (RFAs) have been used for decades to measure the ion energy distribution at surfaces during plasma processing. In the early days, RFAs were used mostly in grounded situations. In more recent times, RFA systems suitable for radio-frequency (RF) bias conditions were developed. The typical design consists of the RFA grid stack embedded in a substrate-like carrier. The grid signals are supplied to the RFA (installed in the plasma chamber) from the airside through RF chokes and vacuum feedthrough located at a vacuum port. The RFA carrier is wired to the vacuum feedthrough on the vacuum side. While this type of solution works well for R&D applications, it is not ideal for a production environment (even for off-line maintenance work) due to the wiring and the need to open the chamber for installation.

There is an increasing demand for plasma measurement and control solutions to cope with the growing complexity of integrated circuit manufacture in the semiconductor industry. Production compatible plasma diagnostic instruments are highly desireable. Silicon wafer based wireless sensors, which measure temperature during the process, have gained the most traction with tool manufacturers and device makers. In this presentation we will present a novel wireless wafer probe with integrated RFA, power supplies and measurement circuitry which can be loaded to the process chamber using the robotic transfer mechanism. RFA sensor data is measured and stored in on-board memory where it can be downloaded later for analysis. This technology has the potential for widespread use in the fab environment.

PS-Contributed On Demand-31 Characterisation of N-Based Plasma-Functionalised Microporous Activated Carbon and Macroporous Cordierite Monoliths for Improved CO_2 Adsorption*, Madhuwanthi Buddhadasa,* Université Libre de Bruxelles, Belgium*; Y. Ali Gómez Rueda, B. Verougstraete,* Vrije Universiteit Brussel, Belgium*; T. Doneux,* Université Libre de Bruxelles, Belgium*; J. Denayer,* Vrije Universiteit Brussel, Belgium*; F. Reniers,* Université Libre de Bruxelles, Belgium

In the battle against global warming, investigating methods to capture and reduce greenhouse gases such as CO_2 has become ever so important in the present time. Due to its many advantages such as solvent-free processing and versatility, plasma techniques are widely being researched for rendering reactive surfaces. In this work, a low-pressure (~80Pa) capacitively coupled RF plasma and an atmospheric-pressure dielectric barrier discharge of ammonia are used to graft nitrogen functionalities onto 3 types of activated carbon (AC) monoliths and a cordierite monolith. The CO_2 adsorption capacity of the monoliths is expected to then improve owing to chemisorption via acid-base interactions between the gas-phase CO_2 molecules and the plasma-immobilised amine groups on the sample surface[1]. Influence of treatment parameters such as plasma power, chamber pressure and sample position in the reactor on N grafting is studied by x-ray photoelectron spectroscopy and optical emission spectroscopy. A N/(N+C) of up to 20% can be detected on both AC and cordierite samples. The chemical composition of the pristine ACs, mainly the inherent oxygen content most likely originating during the synthesis of ACs, is found to influence the N grafting selectivity. In the monolithic structure, depending on the treatment conditions a differential functionalisation of N is observed inside the channels wherein the N content can be reduced by half compared to that present on the outer surface. The low-pressure RF ammonia plasma visibly consists of two distinct regions, a bright violet zone near the powered electrode and a less bright white zone further away from it. The position of the sample in these two regions exhibit a clear difference in the N content, where less N is grafted in the bright region. An influence of the sample size on the surface chemistry is observed which is also reflected in the emission spectra. Accordingly, important insights into plasma surface modification of 3D geometries are highlighted. CO_2 adsorption is characterised by pressure swing adsorption at an isotherm of 30°C. A 27% increase in the adsorption capacity of N-functionalised AC monoliths and at least 20% increase for cordierite monoliths is observed. The adsorption capacity shows a positive dependency on the surface N content. Despite the chemisorption of CO_2, a temperature as low as 30°C under deep vacuum is found to be sufficient for a complete regeneration of the AC monoliths facilitating a low energy intensive regeneration process.

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PS-Contributed On Demand-34 Insights Into the Plasma Catalytic Decomposition of Methane: Role of Atomic O and Surface Species*, Yudong Li,* University of Maryland College Park*; J. Jiang,* University of Minnesota*; M. Hinshelwood,* University of Maryland College Park*; P. Bruggeman,* University of Minnesota*; G. Oehrlein,* University of Maryland College Park

Cold atmospheric pressure plasma generates reactive species that can enhance catalyst-based chemical reactions. Recently, we developed a non-thermal atmospheric pressure plasma jet (APPJ)-catalyst system that enables real-time gas phase and operando surface characterization. This system has been used to study the influence of plasma on the oxidation of CH_4 to CO and CO_2 over a Ni-SiO_2/Al_2O_3 catalyst. In prior work, the gas phase species and surface intermediates corresponding to different plasma chemistries were investigated. In this work, we studied the mechanism of plasma-catalytic CH_4 decomposition by analyzing the correlation between reactive species produced by plasma, gas phase products and surface species. Ar/CH_4 gas was injected downstream of the APPJ near the catalyst where it interacted with the O_2 gas and reactive oxygen species (ROSs) in the Ar/O_2 APPJ effluent. Real-time Fourier-transform infrared spectroscopy was used to quantify the reaction products downstream of the catalyst bed for different conditions. The plasma incident fluxes were measured by mass spectrometry using an identical APPJ operating under the same conditions (although with a substrate containing a sampling orifice in place of a catalyst bed). By varying the plasma feed gas composition, plasma power, and catalyst temperature (25 °C to 500 °C) and correlating the quantified ROSs fluxes with the results of the downstream measurements, we observed a strong correlation of the rates of CH_4 consumption, CO and CO_2 production with the O atom flux incident on the catalyst. This result implies that atomic O plays an essential role for the catalyst enhanced temperature-dependent oxidation of CH_4 to CO and CO_2 for our experimental conditions. We also used in-situ diffuse reflectance infrared Fourier transform spectroscopy to analyze the catalyst surface species. We found that the abundance of surface CO follows that of surface CH_n with plasma at 25 °C, indicating that the CH_n is the precursor species for the formation of surface and gas phase CO. No discernable surface CH_n was observed at 500 ^oC, while surface CO was more pronounced, indicating that the decomposition of CH_4 to CH_n might be the rate-determining step at 500 ^oC. The same phenomena of low surface CH_n and high surface CO coverage have been observed using an Ar/O_2/CH_4 plasma jet. However, when CH_4 is flown through the APPJ, a more intense reaction of CH_4 with oxidizing species is seen, indicating the importance of plasma on the activation of CH_4 for the decomposition reaction. We gratefully acknowledge funding from National Science Foundation (CBET-1703211 and CBET-1703439) and US Department of Energy (DE-SC0020232).

PS-Contributed On Demand-37 Plasmonic Nitridation of Silicon Surface via Plasma-Induced Wavelength-Mixed Gold Nanoparticle Excitation*, Takeshi Kitajima, K. Watanabe, M. Miyake, T. Nakano,* National Defense Academy, Japan

Catalytic surface reactions utilizing gold nanoparticle plasmons have been utilized in various applications in recent years.[1] We have applied hot electrons supplied from gold nanoparticles to plasma surface reactions to use them to form high-quality ultrathin films.[2] We focused on the mixed effect of visible light for plasmon excitation and plasma VUV emission and discovered the effect of green light excitation that promotes radical nitriding.

Au was vapor-deposited on a SiO2 / Si (100) substrate in an ultra-high vacuum chamber with an average thickness of 0.4 nm by electron beam deposition to form Au nanoparticles (C) on the surface. A 30 mTorr N2-inductively coupled plasma was generated in the attached chamber, and the sample was irradiated with N radicals (R) that passed through a 30 line/inch SUS304 single mesh with the configuration shown in Fig. 1 (a) for 5 minutes. A filter and a white LED controlled the wavelength of light (L), and VUV light from N2 plasma was mixed. The reaction condition consisting of the above is RLC. Figure 1 (b) shows the dielectric characteristics of the SiON film {leakage current and EOT (equivalent oxide film thickness) when 1 V is applied}. In green light suitable for Au plasmons, the hot electrons (~ 4 eV) generated by the deexcitation of plasmons enabled the bond conversion from Si-O to Si-N the ultra-thin SiON shows the same characteristics as the thermal oxide film. By mixing VUV, it is possible to increase the film thickness further and reduce leakage. From the above, it is considered that the reaction between the adsorbed N radicals and Si proceeded, and a good quality SiON film was formed by superimposing the photoelectron emission from the VUV light on the hot electron injection from the Au nanoparticles by green light irradiation.

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PS-Contributed On Demand-40 Low-Temperature Deposition Technology of High-Quality and Low-Stress SiO_2 and SiN Films for Photonics Devices Using ECR Plasma*, Masamitsu Toramaru, Y. Jin,* Japan Steel Works, LTD., Japan*; k. Mori, H. Torii, T. Mashita,* JSW AFTY Corp., Japan

Recently, optical modulators using $LiNbO_3$ (LN) or silicon as a substrate and waveguides using SiN films have been actively researched. These light modulators and waveguides require materials that prevent light leakage or absorption to efficiently transport light. Therefore, multilayered substrate of LN/SiO_2/LN and LN/SiO_2/Si for optical modulators, and substrates for optical waveguides with a SiN film on the upper LN layer of the multilayered substrates are also developed. The SiO_2 layer used in an optical modulator is a buffer layer to confine the propagation light to the waveguide. It requires a thickness of several µm and a large refractive index difference from the waveguide material to prevent light leakage in the waveguide. The SiN layer for the waveguide also requires a thickness of hundreds of nm with low optical absorption. However, conventional PECVD has poor reactivity and cannot deposit a high-quality film without external substrate heating. Therefore, we focused on ECR (electron cyclotron resonance) plasma technology to deposit thick SiO_2 and SiN. They are high-density plasmas generated by resonating microwaves and a magnetic field, and they are characterized by high reactivity in a low-temperature process, with minimal damage from low-energy plasma stream irradiation and minimal contamination by electrodeless discharge.

ECR sputtering systems have been used for edge-emitting lasers and surface-emitting lasers, for which high density, flatness and excellent optical properties are required, such as a semiconductor laser AR/HR coating. On the other hand, sputtering systems have poor productivity for µm-order film thicknesses due to their slow deposition rate and high film stress caused by high-quality film.

In order to deposit high-density and low-stress SiO_2 and SiN films with µm-order thicknesses without heating, an ECR-CVD system using ECR plasma for CVD was developed. Then, SiN films using SiH_4 and N_2 as a nitriding source and SiO_2 films using O_2 as an oxidant were deposited by our ECR-CVD system. In the SiN deposition process using N_2 instead of conventional NH_3, it is possible to deposit high-quality SiN films that have less hydrogen and thus can be applied as a waveguide. High-quality SiN and SiO_2 films with refractive indices similar to those of ECR sputtering are obtained at a 200 nm/min deposition rate without substrate heating.

In this presentation, we show that high-quality and low-stress films of SiN and SiO_2 films for photonics devices can be obtained by ECR-CVD, and we report on composite substrates prepared by applying the ECR plasma technology.

PS-Contributed On Demand-43 Automatic Etching-Recipe Optimization in Si Etching with Self-Aligned Quadruple Patterning Masks for Productivity Enhancement by Transfer Learning*, Naoto Takano*, *H. Nakada, T. Ohmori,* Hitachi, Ltd. Research & Development Group, Japan

In semiconductor manufacturing, an etching process with extremely high precision is required because nanometer-order shifts in etching profiles can cause serious problems in the electrical characteristics of the devices. One of the causes of such shifts is a change of the etching chamber stemming from, for example, deterioration of the internal parts over time, replacement of the deteriorated parts with new parts, or replacement of some or all of the parts to upgrade the chamber. So far, to correct such shifts, proficient engineers have reconsidered etching recipes (the control parameters in etchers) on the basis of etching results obtained before and after the chamber changes. However, due to increasingly complicated device structures and the miniaturization of their critical dimensions, the number of parameters in recipes for state-of-the-art devices has increased. Therefore, recipe optimization has become much more difficult. Since there is a shortage of proficient engineers who have the ability to optimize recipes, a decline in manufacturing productivity is inevitable.

To help engineers optimize recipes, we developed a method to automatically optimize recipes by using transfer learning. In this method, first, a regression model between recipes and etching profiles is trained by using former data, namely, etching data obtained before the change of the chamber. Next, the regression model undertakes additional training by transfer learning with small amount of latter data, namely, etching data obtained after the change in the chamber Finally, the optimal recipe is predicted by the regression model that learns both the former and the latter data.

In this study, we applied our method to recipe optimization for Si trenches with 12.5-nm-wide Self-Aligned Quadruple Patterning (SAQP) masks. We used an etcher that had previously had its hardware remodeled to improve its exhaust performance. Due to the hardware remodeling, the etch rate decreased by about 20%. To re-optimize the recipe after the remodeling, we used etching data obtained before and after the remodeling as former and latter data by transfer learning. As a result, we succeeded in obtaining a predicted recipe to achieve almost the same etch rate and etching profile of 12.5-nm-wide Si trenches with an aspect ratio of 10 as before the remodeling. Furthermore, the amount of latter data needed for the recipe prediction was less than 1/3 of that in the supervised-learning based method [1]. Therefore, when the chamber configuration is changed, our method is expected to achieve productivity enhancement.

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PS-Contributed On Demand-46 Plasma Etch Solutions for Defect Reduction in Ultra-Thin Photoresist*, Jihun Park,* Sungkyunkwan University (SKKU), Korea (Republic of)*; S. Kim,* Samsung Electronics, Korea (Republic of)*; G. Yeom,* Sungkyunkwan University (SKKU), Korea (Republic of)

The semiconductor industry aims to manufacture integrated circuits (ICs) with higher density devices in smaller chip areas in order to increase performance while reducing manufacturing costs. To this end, the dimensions of circuits and devices are continuously reduced, and the etch process continues to develop along with photo micro-patterning to overcome the limitations. This trend has led to the use of ultra-thin photoresist (PR) and is putting a burden on the etch process. There are many problems with photo micro-patterning using ultra-thin PR, especially scum cause pattern defects such as abnormal contact, contact not open, contact missing and CD uniformity defects due to local variation. Since this problem can be solved through scum removal, in most cases, the descum step was proceeded during mask etching. However, under the ultra-thin PR condition below 70nm, it is difficult to proceed with the descum step due to the lack of PR margin. So we added the polymer deposition step and used it as a barrier, which allowed the scum to be removed while maintaining the PR margin.

In this paper, we introduce an innovative plasma process technology called DDP (Descum-Deposition-Process) that can remove PR scum while overcoming the insufficient PR margin. This study aimed to improve defects in the contact etch on middle of line (MOL) and applied DDP using CH4 and CHF3 gases to etch ultra-thin PR on SiON. In particular, DDP for high loading deposition and low loading etch can improve local CD variation and pattern defects by increasing the PR margin. In order to verify the effect of the condition, we used SEM equipment (uniformity verification through CD measurement), Defect inspection tool (Defect and not open verification).

As a result, it was confirmed that not open defect and local CD variation is improved.

PS-Contributed On Demand-49 Design of Organosilicon Nano-Membrane at Atmospheric Pressure With a Glow Discharge and New Applications for Electrochemical Devices*, Jacopo Profili,* CHU de Québec-Université Laval Research Centre, Canada*; M. Beauchemin, S. Rousselot,* Université de Montréal, Canada*; L. Martinu,* Polytechnique Montréal, Canada*; M. Dollé, L. Stafford,* Université de Montréal, Canada

In the last few years, researchers around the world have focused on the development of more “eco-friendly” products and sustainable processes. Plasma treatments at atmospheric pressure have gained interest because of their low consumption of chemicals, the dry polymerization mechanisms, as well as the possibility to develop new exotic chemical functionalities on surfaces and interfaces. Although several articles have been written on plasma polymers and their applications, their synthesis on more exotic materials – such as green composites or natural porous substrates – have been only studied by a few authors in the last years. We recently demonstrated how the micro- and nano-porosity can control the physic of the discharge and thus the breakdown mechanisms. Different fragmentation mechanisms and growth modes have also been highlighted depending on the porosity.

These findings have recently been used to control the synthesis of an organosilicon nanomembrane for the modification of “green” composite electrodes used in aqueous batteries.

Here, we report the properties of an organosilicon (SiOxCyHz) thin membrane, obtained by atmospheric pressure dielectric barrier discharge (AP-DBD). The plasma has been used to control the electrochemical stability of a composite layer made from carboxymethyl-cellulose, carbon black and Lithium-based nanoparticles. The synthesized nano-membrane is preventing the electrode loss of electronic percolation and increasing the electro-chemical stability over a prolonged number of cycles in low concentrated aqueous electrolytes. In this study, the physico-chemical properties and electrochemical performance of such electrodes were investigated. The porosity of the nano-membrane has been used to control the diffusion of ions, and limits the natural degradation created by the water molecules inside the electrode. Different organicity levels (Si-CHx band to Si-O-Si in-phase asymmetric stretching band, AS1, ratios) and matrix disorder (AS1 to Si-O-Si out-of-phase asymmetric stretching band, AS2, ratio) have been compared. The results indicate that the plasma membrane sustains numerous cycling without affecting the electrochemical activity. This suggests a reduced degradation of the plasma layer despite the volume variation of the electrodes during the charging/discharge process. To better understand this phenomenon, the mechanical of the organic silicon thin layer obtained in similar conditions at atmospheric pressure has been studied. Adhesion, tribological and mechanical properties were assessed by nanoscratch and depth-sensing indentation measurements. The results suggest compressive stress in the bulk, and energy uptake during depositions. This feature is ascribed to low-energy ion irradiation and surface de-excitation of metastable atoms in the AP-DBD.

PS-Contributed On Demand-52 Optimization Process for the Fabrication of Ultra-Low Loss PECVD Silicon Nitride-on-Insulator Waveguides

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Low-loss silicon nitride (SiN) thin-film is very appealing because it opens possibilities for multi-layer photonic chip fabrication and hybrid integration of optical waveguides [1]. Up to now, the most common low-temperature deposition technique for SiN is plasma-enhanced chemical vapor deposition (PECVD). However, such SiN thin-films usually present significant optical losses at telecommunication wavelengths because of bulk absorption losses due to the presence of significant NH bonds in the SiN materials [2, 3] and scattering losses due to the top and sidewalls roughness [4] of the SiN waveguides after plasma patterning. In this work, we propose to optimize the fabrication process flow of PECVD SiN waveguides in order to achieve ultra-low loss waveguides (<0.5dB/cm). Plasma processes using fluorocarbon plasma chemistries have been optimized to minimize the sidewalls roughness of waveguides during the patterning of two Si-rich SiN materials, with different initial optical indexes, surface roughness, and NH content. Moreover, annealing treatments have been investigated to reduce the hydrogen content. Preliminary results show that the annealing treatments decrease significantly the NH content, while these SiN materials exhibit higher sidewalls roughness after the plasma etching process. Therefore, the plasma process improvement is still going on to reach better sidewalls roughness of the waveguide.

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PS-Contributed On Demand-55 RF Hollow Cathode Discharge: Particle-in-Cell/Monte Carlo Simulation

***Kallol Bera**, X. Li, A. Verma, S. Ganta, S. Rauf,* Applied Materials, Inc.

Radio-frequency (RF) hollow cathode discharge (HCD) plays an important role as a plasma source for material processing in the semiconductor industry. Hollow cathode systems typically consist of an array of small hollow cylindrical holes on the cathode. The plasma in the hollow cavities can become more intense due to the hollow cathode effect (HCE) under certain conditions. A single hollow cathode hole is modeled using Particle-in-Cell/Monte Carlo simulation. In this 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’ velocities are updated and the particles are moved. This PIC code considers particle collisions with each other and with neutral fluid using a Monte Carlo model. Statistics of these collisions are used to determine how electron energy is dissipated in the plasma. We have explored the effect of gas pressure, RF voltage and frequency as well as secondary electron emission on plasma density in the RF HCD using this model. At higher pressure, plasma penetrates inside the hole, leading to HCE enhancement. At high RF voltage, plasma density enhancement is limited as plasma spreads over larger volume. The secondary electron emission as well as RF sheath heating play important role in electron power deposition. To better understand the role of secondary electrons, we have explored different secondary electron emission coefficients at various RF frequencies. In order to determine the collective behavior of an array of hollow cathode holes, a reduced order model based on a neural network is developed utilizing the detailed PIC modeling results. Preliminary results using this reduced order model are presented.

PS-Contributed On Demand-58 Determination of Recombination Coefficients for Hydrogen, Oxygen and Nitrogen Gasses via in-Situ Radical Probe System

***Dren Qerimi**,* University of Illinois at Urbana-Champaign*; D. Ruzic, G. Panici, A. Jain, D. Jacobson,* University of Illinois at Urbana-Champaign, USA

Determination of recombination coefficients of gases on solid surfaces varies depending on the process and environment. Values of recombination coefficients are dependent on factors such as temperature, surface morphology, impurities, chamber and surface thickness. A zero-dimensional plasma model is developed to predict radical densities of hydrogen, oxygen and nitrogen as a function of electron temperature, plasma density and pressure which are measured experimentally. The predicted radical densities are then used to calibrate experimental measurements of averaged temperature difference between two catalytic probes with different surface materials. The radical density measured via in-situ radical probe system is matched with density obtained from plasma model in order to determine the value of recombination coefficient. Recombination coefficient of hydrogen radicals on a gold surface is found to be 0.115±0.018. Recombination coefficients of oxygen and nitrogen on copper are found to be 0.31±0.063 and 0.18±0.034, respectively.

PS-Contributed On Demand-61 Sheath Model for Electromagnetic Simulation of Capacitively Coupled Plasma

***Xiaopu Li**, A. Verma, S. Ganta, K. Bera, S. Rauf,* Applied Materials, Inc.

Capacitively Coupled Plasmas (CCP) are commonly used in semiconductor manufacturing. Electromagnetic (EM) field and power distribution are generally studied in practical reactors assuming bulk plasma as a lossy media with complex conductivity. Since plasma sheath plays an essential role in plasma heating and power deposition, it is critical to incorporate sheath model to capture accurate EM response of CCP reactors. A simple sheath model includes a nonlinear distributed circuit consisting of a capacitor, a diode and a current source. The circuit components are self-consistently solved based on assumptions of Lieberman [1] or Metze, Ernie and Oskam (MEO) [2]. In this study, a simplified CCP reactor is simulated using a FDTD solver coupled to the MEO sheath model. The resulted EM field distribution shows multiple harmonics due to the nonlinearity of the sheath. An electrical asymmetry is achieved using unequal electrode areas or modulated waveform. The reactor impedance is calculated from lumped voltage and current, and is compared to the result of a fluid-based plasma model. Additionally, a reduced order sheath model is studied numerically from full-scale plasma model, which provides a promising way to handle realistic CCP reactors.

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PS-Contributed On Demand-64 Characterization of Reversed Arc Hydrocarbon Plasma in Material Synthesis

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The reversed arc plasma-enhanced PECVD reactor utilizes the reversed arc discharge conducted between the remote anode positioned in the high-pressure plasma processing compartment connected to the plasma-creating gas supply line and the primary cathode positioned in the low-pressure compartment connected to the pumping system. The anodic plasma processing compartment was separated from the primary arc compartment by the diaphragm with the small orifice. The high-current reversed arc discharge was generated in a mixture of hydrogen and hydrocarbons with argon at moderate pressures ranging from 1 to 100 Torr in compositions typical in the synthesis of diamonds and related materials. The effect of gas pressure on the current-voltage characteristics of the reversed arc discharge was studied at different plasma-creating gas mixtures. The electrically floated substrates such as pieces of Si wafers were positioned either on the surface of the flat remote anode disk, separated from the anode by sapphire wafer, or, alternatively, were suspended within the current-carrier arc plasma column on thin, high-temperature dielectric cable. The temperature of the substrate was measured either by thermocouples or by IR pyrometer. In the spectrum of Ar-H_2-CH_4 reversed arc plasma column in the wavelength range of 400-620 nm there are CH, C_2, and H_2 molecular bands, in addition to Hβ, Hγ, and Hδ lines of atomic hydrogen. The dissociation degree of molecular hydrogen was estimated using the optical actinometry method from intensity ratio $I_{H\alpha}/I_{ArI}$ of the H_α and ArI 750 nm lines, showing the dissociation degree of hydrogen in the arc plasma is about 15-20%. The reversed arc plasma column and its interaction with substrates were modeled in an axially-symmetrical one fluid, one temperature approximation using commercial COMSOL FEM software. The dissociation of the hydrogen across the discharge tube was calculated by the thermal dissociation model, based on the advection-diffusion-reaction (ADR) equation for atomic hydrogen produced by Ar or H_2 impact and lost in three-body recombination, and via LTE calculation. The results of the comparison of hydrogen dissociation degree across the arc column demonstrate a high degree of dissociation of molecular hydrogen in reversed arc plasma in reasonably good agreement both with experimental findings and between two modeling approaches. The results obtained on the interaction of reversed arc plasma with substrates suspended in the arc column were applied to the description of the dusty reversed arc plasma consisting of spherical particles uniformly distributed across the reactor channel. It was found that the energy effectiveness of the treatment of micropowder in reversed arc plasma can exceed 90%.

PS-Contributed On Demand-67 Molecular Analysis of Plasma-Induced Germination Improvement of Rice Seeds With High-Temperature Stress Damage*, **Kazunori Koga**, Y. Ishibashi,* Kyushu University, Japan*; C. Suriyasak,* Kyushu University, Japan, Thailand*; T. Okumura, H. Tanaka,* Kyushu University, Japan*; P. Attri,* Kyushu University, Japan, India*; K. Matsuo, D. Yamashita, N. Itagaki, K. Kamataki, M. Shiratani,* Kyushu University, Japan

High-temperature stress damage during the ear ripening of rice (Oryza sativa L.) due to global warming is an important issue of the food crisis. The seeds of rice that experienced high temperatures around above 30 oC from flowering to harvest show delayed germination. Improvement of germination characteristics is an important issue. So far, we have found atmospheric pressure dielectric barrier discharge (DBD) plasma irradiation to seeds promotes germination and growth and increases yield [1,2]. Here, we report plasma-induced germination improvement of rice seeds with high-temperature stress damage.

In the experiment, we employed japonica rice seeds that were harvested under a high-temperature condition of 30 oC from flowering to harvest periods. The harvest year was 2017. They were stored in a freezer at -30 oC for 3 years after their harvest. They were left at room temperature for 1 day before plasma irradiation, and then plasma irradiation was performed using a scalable DBD device [1]. 100 seeds were placed in the area of 4x4 cm2 under the center of the discharge electrode, and the gap between the electrode and the seed was 3 mm. The discharge voltage was 7.0 kVpp. The plasma irradiation was carried out at room ambient temperature and the humidity of 40-60% rh. To avoid temperature rise of seeds during plasma irradiation, 10 s plasma ON and 50 s plasma OFF were repeated 18 times. The total discharge time was 3 min.

We measured 5 sets of germination curves of 30 seeds. The germination rate of seeds with high-temperature damage was 25% at 72 hours after the start of water uptake, whereas that of plasma-irradiated seeds with high-temperature damage improved to 40%. We also measured gene expression of OsAmy1C in a gene group of alpha-amylase which hydrolyze the starch in the endosperm into sugars during seed germination [3]. The variation in the expression of OsAmy1C corresponds to the germination characteristics.

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PS-Contributed On Demand-70 As-grown Crystalline β-Ga2O3 Films Obtained at Low Temperatures via in Situ Atomic Layer-by-layer Plasma Processing*, **Saidjafarzoda Ilhom**, A. Mohammad, D. Shukla, J. Grasso, B. Willis, A. Okyay, N. Biyikli,* University of Connecticut

Wide bandgap (WBG) semiconductors, such as GaN and SiC make the backbone of high-power high-frequency electronic devices, such as in smart vehicles and 5th generation (5G) communication technology. However, production complexity and high-cost of these materials make such technologies less widespread. Gallium oxide (Ga_2O_3) is an emerging WBG semiconductor recently attracting great research attention due to its superior electrical properties. To compete against the mature WBG materials which are grown typically at > 1000 °C, a substantially lower temperature deposition technique for crystalline Ga_2O_3 is critical particularly for its integration with temperature-sensitive substrates or devices. Here, we report on the low-temperature growth of crystalline Ga_2O_3 films on Si, sapphire, glass, and Kapton substrates via hollow-cathode plasma-assisted atomic layer deposition (ALD). Films were deposited using triethylgallium (TEG) and Ar/O_2 plasma as metal precursor and oxygen co-reactant, respectively. Growth experiments have been performed at 150 – 240 °C substrate temperature and 30 – 200 W rf-power range. 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 varied over 50 – 300 W rf-power. The thickness of the films without Ar-annealing stage, ranged between 20.74 – 39.30 nm and as-grown refractive indices were between 1.75 - 1.67 within the scanned plasma power range. XRD showed that Ga_2O_3 films grown without *in situ* plasma annealing exhibited amorphous character irrespective of both substrate temperature and rf-power. Though, with the incorporation of the *in situ* Ar-annealing step the thickness of the films ranged between 22.9 – 31.4 nm with refractive indices of 1.75 – 1.79. The increased refractive index (1.79) and reduced thickness gain (31.4 nm) at 250 W Ar-annealing power indicates possible densification and crystallization of the films. Indeed, XRD and XRR confirmed that *in situ* Ar-plasma treated films grow in a monoclinic β-Ga_2O_3 crystal phase with further improving crystallinity and film density (from 5.07 to 5.60 g/cm^3) with increasing Ar-annealing plasma power. X-ray photoelectron spectroscopy study of the β-Ga_2O_3sample grown under optimal *in situ* plasma annealing power (250 W) revealed near-ideal film stoichiometry (O/Ga of ~1.44) with relatively low carbon content (~5 at. %); whereas, 50 W rf-power treated film was highly non-stoichiometric (O/Ga of ~2.31) with considerably elevated carbon content. Our work demonstrates the effectiveness of *in situ* Ar-plasma annealing process to transform amorphous WBG oxide semiconductors into crystalline films without needing high-temperature post-deposition annealing treatments, which are detrimental to low-temperature sensitive substrates.

PS-Contributed On Demand-73 Computational Optimization and Reduced Order Modeling of Plasma Chemistry in Fluid Plasma Models*, **Sathya S Ganta**, X. Li, K. Bera, S. Rauf,* Applied Materials, Inc.

Fluid plasma modeling enables us to accurately capture the plasma behavior in capacitively and inductively coupled plasma chambers in low to moderately high pressure (>30 milli Torr) regime. Once validated with measurements, these models can be used to optimize the chamber design and process conditions required to obtain the desired fluxes and energies to the wafer which decide process output. Therefore, these models are vital to the semiconductor processing industry. In applications where the plasma chemistry constitutes a large number of chemical reactions and/or species, the computational cost of fluid simulation can be prohibitively high. In this paper, we present an effective methodology to optimize the plasma chemistry by removing the unwanted chemical reactions and species without losing model accuracy. The unwanted chemical reactions and species are specific to a given range of process parameters (pressure, power, electrode spacing, etc.) and are identified using sensitivity analysis. The methodology also enables us to develop reduced order plasma chemistry models with varying degrees of accuracy by analyzing reaction pathways before and after optimization. The optimized reduced order chemistry model is utilized for faster computation of the fluxes and energies to the wafer. These reduced order models can be vital tools to perform efficient mixed-fidelity optimization of process conditions over the range of design and process parameters.

PS-Contributed On Demand-76 Fluorocarbon Plasma Erosion Behavior of Heraeus Black Quartz*, **Mark Stamminger**,* Heraeus Quarzglas GmbH & Co. KG, Germany*; K. Noesges, T. Mussenbrock,* Ruhr University Bochum, Germany*; A. Goetzendorfer, B. Weisenseel,* Heraeus Quarzglas GmbH & Co. KG, Germany

A composite material, Heraeus Black Quartz (HBQ), composed of a silica glass matrix embedded with silicon microparticles, has applications in semiconductor processing systems due to its unique thermal properties and its chemical compatibility with the ultrapure environments used. A potential future application could include use in low-temperature plasma etching reactors. In this work, the fluorocarbon plasma erosion behavior of HBQ materials containing up to 20% silicon by weight was studied in a commercial inductively-coupled plasma reactor at typical processing pressures of 1 to 3 Pa, and for a range of CF_4/Ar ratios. In general, it was found that the silicon microparticles were etched out faster than the surrounding glass matrix. Under these plasma conditions, the overall erosion resistance of the composite HBQ materials was found to be somewhat lower than that of pure silica glass, but substantially higher than that of pure silicon. In order to better understand the internal plasma conditions prevailing during the experiments, the plasma reactor was modelled with the Hybrid Plasma Equipment Model (HPEM) [1]. Fluxes of relevant chemical species such as neutral fluorine atoms or positive ions such as CF_3^+ or Ar^+ to the sample surfaces were determined from the model. Lower chamber pressures lead to higher positive ion and fluorine atom fluxes in the model, which contribute to higher erosion rates of both the silicon microparticles and the silica glass matrix. At higher pressures or higher CF_4 contents of the plasma, the plasma model shows a higher ratio of fluorine atom flux to positive ion flux toward the sample surfaces, which condition favors etching of the silicon microparticles over the silica glass matrix. These results on the erosion behavior of Heraeus Black Quartz are useful for plasma etching systems designers in choosing appropriate materials for chamber components.

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PS-Contributed On Demand-79 Surface and Plasma Characterization of a Self-Limited Two Step Etch Process for SiN Spacer Etching Applications*, Nicolas A. Loubet,* LTM-CNRS, France*; C. Jenny,* STMicroelectronics, France*; C. Petit-Etienne, E. Pargon,* LTM-CNRS, France

Highly selective and anisotropic silicon nitride spacer etching can be achieved through a self-limited two-step process introduced in recent years. The first step is an anisotropic modification via light ion implantation, typically helium or hydrogen, done by a capacitive plasma (CCP) discharge. It is followed by a selective removal performed by exposure to a remote NF3/NH3/He plasma discharge (RP), which consumes the surface by formation of a (NH4)2SiF6 salt layer. The two steps are performed in the same reactor and can thus be cycled1. By monitoring the silicon nitride thickness via in situ kinetic ellipsometry during the RP process it has been shown that the etching starts after an incubation time on non-implanted (vertical) surface. On implanted surfaces, several implant types have been investigated (H2, O2, N2, NH3, He) and the results show that only H-based and He plasma during the first step suppress this incubation time, suggesting that a specific surface state favor neutrals adsorption and the subsequent etching during the RP process. This etch activation not only offers a process window with high selectivity between implanted and non-implanted but also highlights that the surface/plasma interaction are driving the etch during the second step. The Surface state after the first step was characterized using several techniques including: Time of flight secondary ion mass spectroscopy (Tof-SiMS), X-ray Photoelectron spectroscopy (XPS) and X-ray reflectometry (XRR). In order to further the understanding of the etch mechanisms and plasma/surface interactions, plasma characterizations techniques were performed. The Energy distribution and chemical nature of the ions involved in the modification step were studied using Retarding field energy analyzer (RFEA). Using Vacuum ultraviolet absorption spectroscopy (VUVAS), the neutral species present in the remote plasma discharge can be identified and quantified2. Among NF3 and NH3, the presence of HF was detected and could be a potential precursor to the salt formation. Analyzing the gas phase composition for different NF3/NH3 ratios showed that different regime of HF production exits. Those results will be correlated to the etch kinetics of silicon nitride, silicon oxide and silicon obtained by in-situ ellipsometry. A deeper understanding of the gas phase composition and etch activation mechanisms allows to tune the two steps in order to increase selectivity and ultimately optimize the process.

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PS-Contributed On Demand-82 Molecular Dynamics Study on Multi-Steps Plasma-Assisted Atomic Layer Etching of Silicon Nitride*, Jomar Tercero,* University of the Philippines*; A. Hirata,* Sony Semiconductor Solutions Corporation, Japan*; M. Isobe,* Osaka University, Japan*; M. Fukasawa,* Sony Semiconductor Solutions Corporation, Japan*; M. Vasquez,* University of the Philippines*; S. Hamaguchi,* Osaka University, Japan

Atomic-scale precision and control are essential in the etching processes used for the manufacturing of sub-10nm-scale advanced semiconductor devices [1-3]. For such etching processes, the industry normally employs plasma-based processing techniques to achieve near-atomic layer removal of surface materials with low damage to the underlying surface. This process is known as the plasma-assisted atomic layer etching (ALE). A proper understanding of ALE is crucial to develop a well-controlled method to obtain a good selectivity, uniformity, and directionality of such etching processes. Recently, it has been reported that ALE of silicon nitride (SiN) with alternating adsorption of hydrofluorocarbon (HFC) radicals and desorption via Ar^+ ion bombardment induces an etch stop. The etch stop is caused by the accumulation of C atoms on the surface that an Ar^+ ion-based desorption step cannot completely remove [4]. To solve this problem, a multi-step ALE process was proposed to achieve a stable SiN ALE by combining SiN/SiO_2 ALE. This was performed by introducing O_2 plasma irradiation to remove the remaining carbon layer completely [5]. However, as a result, surface oxidation forms a SiO_2 layer, which may be removed by SiO_2 ALE, which consists of the adsorption step of C_xF_y radicals and the subsequent desorption step of the fluorocarbon modified layer by Ar^+ bombardment. With this approach, SiN ALE can be achieved. In this study, molecular dynamics (MD) simulations were used to analyze the multi-step ALE of SiN ALE with an irradiation step of O radicals to remove the excess carbon layer formed during the hydrofluorocarbon desorption step.

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PS-Contributed On Demand-85 Two-Dimensional Particle-in-Cell Modeling of Low Pressure, High Voltage Capacitively Coupled Ar Plasmas*, Amanda Lietz,* Sandia National Laboratories*; P. Tian, J. Kenney, S. Rauf,* Applied Materials, Inc.*; M. Hopkins,* Sandia National Laboratories

Multi-frequency capacitively coupled discharges with relatively low pressure (mTorr) and high bias voltage (kV) are currently of interest for high aspect ratio etching. Unfortunately, this regime poses significant challenges for computational modeling. At these low pressures, fluid models are no longer valid, and a fully kinetic model is required. At these high bias voltages, the high electron velocities severely limit the simulation timestep. As a result, most of the computational studies in this regime have focused on one-dimensional simulations. In this study, two-dimensional simulations of a capacitively coupled reactor with Cartesian symmetry were performed for an Ar plasma at 10 mTorr with bias voltages exceeding 1 kV applied at 2 MHz. The plasma is generated by 2 kV applied at 40 MHz. Aleph, a massively-parallel particle-in-cell direct simulation Monte Carlo code was used to address this problem with a fully kinetic approach. The plasma dynamics, including the plasma density and sheath profile at various pressures, and the resulting ion energy and angular distributions are discussed.

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PS-Contributed On Demand-88 Modeling Capacitively Coupled Plasmas With Nanosecond Pulsed Bias Voltages*, Amanda Lietz,* Sandia National Laboratories*; J. Prager,* Eagle Harbor Technologies*; M. Hopkins,* Sandia National Laboratories

Custom waveforms in capacitively coupled plasma reactors may provide increased control of ion energy and angular distributions. This improved control could enable improvements in etch rate and feature quality, *especially in high aspect ratio etching. New developments in high voltage pulsers are now making it feasible to apply short high voltage pulses with peak power that is sufficient for modern etching reactors. In this study, we model the effects of 100 ns voltage pulses up to 5 kV on plasma dynamics and the resulting ion energy and angular distributions. Aleph, a massively-parallel particle-in-cell direct simulation Monte Carlo simulation tool, was used to model an Ar plasma in one-dimensional simulations. A standard sinusoidal voltage was applied to one electrode, and custom voltage pulses were applied to the other electrode. The resulting plasma and sheath dynamics, as well as their effect on the ion energy distributions are discussed. The results are compared with a standard sinusoidal voltage.*

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

PS-Contributed On Demand-91 Microplasma-Assisted Atomic Layer Deposition and Etching Free Patterning of Ga_2O_3 Film with Enhanced DUV Photoresponse*, **Jinhong Kim**, A. Micronov,* University of Illinois at Urbana Champaign*; D. Sievers,* University of Illinois Urbana Champaign*; S. Park,* University of Illinois at Urbana Champaign*; J. Eden,* University of illinois Urbana Champaign

Gallium oxide (Ga_2O_3) thin film has been deposited on the silicon substrate by arrays of microcavity plasmas enhanced atomic layer deposition (MALD) using trimethylgallium and oxygen plasma. Due to the complete reaction between precursors, the gallium and oxygenstoichiometric ratio for amorphous Ga_2O_3 films has been measured by EDX and RBS to be ~ 1.48 ± 0.2, demonstrating that negligible levels of impurities and oxygen vacancies exist in the films. The optical transmittance of amorphous Ga_2O_3 and β-Ga_2O_3 thin films measured by Varian Cary 5000 UV-VIS spectrophotometer show ~ 95% and 100% transmittance in a range of ~ 250 nm to 500 nm, respectively. The crystallinity of β-Ga_2O_3 thin film after post-annealing with a rapid thermal anneal (RTA) system was investigated by X-ray diffraction (XRD) and transmission electron microscope (TEM). Based on the Tauc law calculation, the optical bandgap of Ga_2O_3 thin film was calculated to be ~ 4.9eV, corresponding to 254 nm illumination. As a proof-of-concept experiment, deep-ultraviolet (DUV) photodetector with metal-semiconductor-metal (MSM) structure was fabricated using MALD for Ga_2O_3 film deposition and metal contact (Ni/Au) was deposited by E-beam evaporator. Amorphous Ga_2O_3 -grown at 300 K exhibited higher responsivity at 254 nm wavelength. Owing to the unique characteristic of MALD, the patterning of Ga_2O_3 films with conventional photoresist and lift-off processing is now a viable option without additional etching process. MALD patterning process introduced here eliminates the need for plasma etching (such as reactive ion processes) and its concomitant damage to sensitive materials. The dark current of DUV photodetector was ~ 10^{-9} A, indicating minimized leakage current from Ga_2O_3 film. The photocurrent with a plateau surface detector was ~ 10^{-6} A and it was increased to ~ 5×10^{-6} A with the periodic stipe/square-patterned interface due to the increased surface volume ratio. The demonstrated ability of MALD to use the plasma source with fragile materials affords the opportunity to leverage well-developed photoresists and lift-off techniques in that patterning films and reducing fabrication steps for layered structures. The unique properties of microcavity plasmas and the confinement of the microplasma electric field allows for nonequilibrium concentrations of radicals and molecular species to interrupt on the substrate in an environment that is essentially field-free and, therefore, exempt from damage arising from ion impact at the substrate.

PS-Contributed On Demand-94 A Mechanistic Approach to Tune Plasma Sintering Parameters for Enhancing Connectivity of Printed Nanoparticles*, **Nazli Turan**, M. Saeidi-Javash , Y. Zhang, D. Go,* University of Notre Dame

Recent developments in additive manufacturing have enabled printing of colloidal nanoparticles for diverse technologies, including energy conversion and storage, sensing, and electronics. Atmospheric pressure, ambient temperature plasmas have become a promising candidate for material processing because they eliminate needs for pressurizing and heating equipment while providing energetic and reactive species that can initiate surface modifications (*e.g.* sintering) at a plasma-surface interface, including thin film nanoparticle assemblies, enhancing material properties (*e.g.* conductivity) in a non-destructive and functional way. Here, we propose a mechanistic approach to plasma jet sintering that correlates plasma parameters (*e.g.* power and flow rate) with the activation energy barrier for surface diffusion, which we identify as the dominant mass transport path leading to a densified structure. We demonstrate an electrical conductivity as high as 1.1×10^6 S/m (2% of bulk silver conductivity) for printed silver films on glass sintered at atmospheric conditions in which the surface temperature stays below 50 °C. Based on the analysis of specific energy input to argon and helium atoms, we calculated an energy barrier of 1.2 eV that is required to be overcome prior to sintering. These results highlight a future direction where additive manufacturing of electronic devices can be achieved on low-melting point materials at ambient conditions and provide a way that we can tune the plasma parameters to trigger effective mass transport between surface particles.

PS-Contributed On Demand-97 Molecular Beam Mass Spectrometry to Measure Absolute Densities of Ions, Vibrationally and Electronically Excited Species in Atmospheric Pressure Plasmas*, **Jingkai Jiang**, Y. Aranda Gonzalvo, P. Bruggeman,* University of Minnesota

Molecular beam mass spectrometry (MBMS) is widely used as a diagnostic method in plasma processing with the ability to detect a large range of different species and to measure species fluxes or densities at a substrate [1]. The latter enables directly linking the obtained fluxes with plasma-surface interaction studies. In this work, we extended the capability of MBMS by developing detection and calibration approaches for the absolute measurement of singlet delta oxygen, $O_2(a^1\Delta_g)$ the first electronically-excited state of O_2, vibrationally-excited nitrogen $N_2(v)$, as well as the absolute density of ions. The measurements are performed in an atmospheric pressure plasma jet (APPJ) operating in Ar with admixtures of O_2 and N_2.

The MBMS measurements of $O_2(a^1\Delta_g)$ showed that $O_2(a^1\Delta_g)$ is the dominant reactive species in the effluent of an atmospheric pressure plasma jet (APPJ) [2]. The ability to measure axial and radial profiles of $O_2(a^1\Delta_g)$ impinging on a substrate in the effluent of the APPJ is a key advantage of the MBMS diagnostic method over well-established optical diagnostics. The large flux of $O_2(a^1\Delta_g)$ has been directly linked to the effective inactivation of virus by this APPJ.

The spatially resolved measurements of $N_2(v)$ in the effluent of an APPJ were enabled by fitting the mass spectrometry signals with the electron-impact ionization cross sections of $N_2(v)$ as a function of electron energy, assuming a Treanor-like vibrational distribution function. The approach provides a complementary diagnostic technique for detecting $N_2(v)$ near substrates with excellent spatial resolution and detection limits, and also shows that RF-driven plasmas can produce large fluxes of vibrationally-excited nitrogen that is reported to be important in plasma catalysis.

Absolute densities of positive ions in the effluents of an APPJ were obtained through calibration with a dc corona discharge with a well-known current density profile [3]. Positive ion densities in the effluent of the APPJ were found to be more than 4 orders of magnitudes lower than the densities of the dominant reactive neutral species (O, $O_2(a^1\Delta_g)$, O_3) in the afterglow region suggesting that plasma-surface interactions in this case are dominantly due to neutral radical interactions.

These results are examples of extended diagnostic capability in atmospheric pressure plasma that have a large potential to enable a better understanding of plasma-surface interactions.

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PS-Contributed On Demand-100 EUV Induced Formation of Hydrogen Plasmas at Low Pressure*, **Tugba Piskin**,* University of Michigan*; H. Lee, S. Nam,* Samsung Electronics Co., Inc., Korea (Republic of)*; M. Kushner,* University of Michigan

The continuing decrease in feature size in microelectronics processing has produced a progressive decrease in the wavelengths for photolithography. The recent deployment of Extreme Ultra-Violet (EUV) lithography systems with photon wavelengths of 13.5 nm are intended to enable feature sizes to below 10 nm. One method to produce EUV photon beams is to ablate and ionize tin droplets with pulsed lasers.A drawback of this method is that tin vapor and ions contaminate the chamber and can damage the collector mirrors. By filling the chamber with low-pressure H_2 gas that does not significantly absorb the EUV photons, a low density plasma is produced by the EUV photon flux that dissociates and ionizes hydrogen.Tin deposits on optics are then etched by H atoms and ions producing stannane (SnH_4), which can be pumped away [1]. The EUV photon energy (92 eV) is far in excess of the ionization and dissociation thresholds of H_2, which results in energetic photo-electrons and, through the Franck-Condon effect, energetic dissociation fragments.There is a careful balance that is required to produce sufficient H atoms to clean the optics of Sn deposits, while not having energetic ions that might damage the surfaces of the collector and mirror.

In this paper, we discuss results from a computational investigation of the plasma formation that occurs by EUV photon beams (13.5 nm, 92 eV) passing through low pressure H_2.This investigation was performed using the Hybrid Plasma Equipment Model (HPEM) which was modified to capture the heating of electrons and ions from photoionization reactions and to produce hydrogen plasma formation only from photon beams. The outcomes of the simulation are the densities of radicals, ions, and excited species, and their fluxes (including energy-and-angular distributions) to the chamber walls. For pressures of a few to tens Pa, and EUV powers of tens to hundreds Watts, the dominant ion is typically H_3^+ while an electron temperature of 4-5 eV produces a plasma potential of up to 20 V.This produces ion energies onto surfaces of 15 – 20 eV.A large density of vibrationally excited H_2 enables a significant production of negative hydrogen ions.The consequences of pulse repetition frequency, pressure and photon intensity on plasma properties will be discussed.

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PS-Contributed On Demand-103 Molecular Dynamics Simulation of Oxide-Nitride Layer Etching by Fluorocarbon Plasmas

Charisse Marie Cagomoc*, M. Isobe, S. Hamaguchi,* Osaka University, Japan*; E. Hudson,* Lam Research Corporation

Due to the development of technologies that require heavy data usage, the demand for 3D NAND devices with better efficiency and larger memory capacity is still not ceasing. 3D NAND devices are founded upon stacking of alternating oxide-nitride or oxide-silicon layers. The higher the number of stacked layers, the higher the storage capacity becomes. In this study, we have performed molecular dynamics (MD) simulation of reactive ion etching of silicon dioxide (SiO_2) and silicon nitride (Si_3N_4) bilayer by CF_3^+ ions, which represent typical reactive ions from fluorocarbon plasma. A 5nm-thick SiO_2 layer was placed on top of a Si_3N_4 layer and bombarded by CF_3^+ ions with an energy ranging from 200eV to 2000eV, which can reveal the reaction mechanism as etching transitions from SiO_2 to Si_3N_4. It is found that, for 200eV to 1000eV, the change in depth of the substrate as a function of the ion dosage shows two distinct slopes as the etching passes through the SiO_2-Si_3N_4 interface. Though the difference in the slopes becomes less apparent as energy increases, this shows that a 5nm-thick SiO_2 layer could still be treated as a separate substrate by ions with energies up to 1000eV. However, at 2000eV, the penetration depth of the ion reaches up to 6nm, which is thicker than the initial SiO_2 thickness. At this energy, the etch rates of SiO_2 and Si_3N_4 are nearly the same. It is also found that, for 200eV to 1000eV, the amount of carbon left on the SiO_2 layer during the etching process increases rapidly as the SiO_2 etching transitions to Si_3N_4 etching. This was not observed at 2000eV as the formation of a thick damaged layer creates a mixed SiON material whose depth is comparable with those of SiO_2 and Si_3N_4 (i.e., ONO) layers of the 3D NAND structure.

PS-Contributed On Demand-106 Improving the Hydrophilic Properties of Pet Textiles Using Atmospheric Dbd and RF Plasma Torch

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The textile industry is constantly searching for rapid ways to improve the properties of textile surfaces. For example, polyester fabrics made of poly(ethylene terephthalate) (PET) are widely used in the clothing field and in the biomedical field (respiratory masks, wounds dressings). However, they are very hydrophobic and may display an important amount of static charges at their surface, generating discomfort in wear, but also making them difficult to dye, clean or coat[1,2].

In the hydrophilization of textiles surfaces, plasma technologies represent a simple and eco-friendly alternative to the traditional alkaline soda process that consume a lot of chemicals, water and energy[3,4]. Plasmas can generate the oxidation and etching of textile fibers, increasing their surface energy, hence their wettability and adhesion to other materials. Originally developed and used in this field at low pressure[5], they now tend to be performed at atmospheric pressure to avoid the use of pumping systems, and make them implementable in continuous on-line productions[6,7].

The present work aims at contributing to a better understanding and control of the reaction mechanisms involved in the hydrophilization of textiles by atmospheric plasmas. In particular, the use of a dielectric barrier discharge (DBD) and a RF plasma torch was investigated for the modification ofPET fabric surface properties. Different plasma parameters such as the addition of reactive gases to the discharge or the exposure time were varied, and the resulting wettability of the treated textile was studied by the means of water contact angles (WCA) measurements and wicking tests. Surface composition of the fabric was also examined by X-ray Photoelectron Spectroscopy (XPS). It was found that a complete wicking of PET textile could be obtained after 20 s of Ar plasma torch treatment, and only 10 s when adding O_2, and after 30 s of Ar DBD treatment. These results could be associated to the plasma functionalization and etching phenomena.

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PS-Contributed On Demand-109 One-Step Synthesis of Chemically Patterned Thin Films via Immobilization of Plasma Filaments in an AP-DBD

Annaëlle Demaude, Université libre de Bruxelles, Belgium*; K. Baert,* Vrije Universiteit Brussel, Belgium*; D. Petitjean, E. Goormaghtigh,* Université Libre de Bruxelles, Belgium*; T. Hauffman,* Vrije Universiteit Brussel, Belgium*; M. Gordon,* University of California Santa Barbara*; F. Reniers,* Université Libre de Bruxelles, Belgium

The ability to locally modify surfaces chemistry and/or topography at sub-millimeter scales is needed in a broad range of fields such as biology, microfluidics, liquid transport, electronics, and photonics[1–4]. Methods to synthetize such surfaces are numerous, but generally involve many steps and/or require low pressure environments[5–7] (layer deposition with masks, lift-off processes, mold to substrate imprinting, ion beams, etc.). Among them, plasma-based technologies, and more particularly, dielectric barrier discharges at atmospheric pressure (AP-DBD) are attractive tools because of their ability to etch or deposit thin films over large areas at scale without complex vacuum systems.

Here, we demonstrate how chemically and topographically patterned thin films can be synthesized by immobilizing filaments in a DBD discharge operating with an organic precursor/Ar mixture. Using different precursors, under different burst modes, and on different substrates (silicon wafer, glass, and aluminum), the stationary filaments led to different patterns. In each case, thicker circular areas of sub-mm diameter (aka ‘spots’) were visible where filaments were ignited on the substrate. Profilometry revealed different thickness, roughness, size and shape of the spots, depending on the plasma parameters, which ultimately depend on the distribution of surface discharges generated around the filaments, as observed with high-speed imaging. XPS and IR analysis also highlighted differences in the molecular structure/composition of spots versus areas between them. This could, in great part, explain the different wettability patterns obtained when using propargyl methacrylate as a precursor (hydrophilic spots with hydrophobic surrounding area or *vice versa*). Overall, this work demonstrates a new, simple path to locally tune the chemistry and topography of surfaces using atmospheric pressure DBD discharges.

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PS-Contributed On Demand-112 Control of the process environment for HfO-based RRAM device formation*, Hiroyuki Miyazoe,* IBM T.J. Watson Research Center*; D. Koty,* TEL Technology Center, America, LLC*; H. Yan, N. Gong, M. Hopstaken, E. Cartier, J. Ott,* IBM T.J. Watson Research Center*; Q. Yang, A. Mosden,* TEL Technology Center, America, LLC*; T. Ando, S. Engelmann, E. Joseph,* IBM T.J. Watson Research Center

Resistive random access memory (RRAM) have been widely considered as a next-generation nonvolatile memory and analog computing applications due to fast write and read access, low power consumption and process compatibility to the conventional CMOS technologies [i,ii]. Oxygen vacancies in metal oxide (MO) film are considered as a driving force for HfO-based RRAM switching [iii]. Therefore, the control of oxygen in the device, and its process chemistry are critical for the performance of RRAM. In this work, we evaluated the control of the process environment for RRAM device formation using low temperature diffusion plasmas. First, we evaluated different etch methodologies and chemistries for HfO using continuous plasma and gas cyclic etching. We observed different RRAM size dependence in switching resistance with the devices smaller than 1um, suggesting controlled sidewall damage on top metal electrode during HfO etch. Second, we compared O2-containing and O2-free hydrofluorocarbon etch processes with similar etch rate and with similar selectivity to SiOx, poly-Si and spin-on organic under layer. Exposure of O2 containing plasma to the top electrode of RRAM resulted in the increase of the device forming voltage, while O2 free plasma chemistry did not show a significant change. Damage-free SiN etching may be attributed to a good control of the plasma etch chemistry and to the low-damaging nature of the diffusion plasma. These process learnings envision the ability and controllability of RRAM as the next-generation devices.

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PS-Contributed On Demand-115 III-V/Ge Heterostructure Plasma Etching and Passivation With a Single Plasma Process for Low-Damage Multijunction Solar Cell Fabrication*, Mathieu de Lafontaine,* Laboratoire des Technologies de la Microelectronique, CNRS-LTM, France, Canada*; E. Pargon, G. Gay, C. Petit-Etienne,* Laboratoire des Technologies de la Microelectronique, CNRS-LTM, France*; J. Barnes, N. Rochat,* CEA, LETI, MINATEC Campus, France*; M. Volatier, A. Jaouad, S. Fafard, V. Aimez, M. Darnon,* Laboratoire Nanotechnologies Nanosystèmes (LN2) - CNRS UMI-3463 Institut Interdisciplinaire d'Innovation Technologique (3IT), Université de Sherbrooke, Canada

Over the past few years, plasma etching processes were the object of a growing interest for multijunction solar cell fabrication. They are used to etch mesas to electrically isolate one cell from another but also to plasma-dice the cells from the wafer. More recently, plasma etching was also used to pattern via-hole on multijunction heterostructures in order to fabricate solar cells with through cell via contacts. This architecture aims to increase the multijunction solar cell efficiency by 3% and the power yield per wafer by 20% by transferring the front side contact to the backside using insulated and metallized vias. For all these applications, the task is challenging as dozens of epitaxial layers must be anisotropically etched with low roughness and minimal damage to ensure optimal cell performance. In this abstract, a plasma process is proposed to both etch anisotropically the III-V/Ge heterostructure while passivating the etched sidewall in order to maximize the cell efficiency.

The epiwafers consist of a III-V heterostructure (InGaP, (In)GaAs, GaAs, AlInP, AlGaAs, AlGaInP layers and quantum dots) epitaxially grown on Ge substrate. The etching processes consist of a $SiCl_4/H_2$ plasma performed in an inductively coupled plasma reactor at high bias power. The etch morphology, the sidewall composition and the cell performance were all studied as a function of the hydrogen fraction in the plasma (0%, up to 67% of the total gas flow). Cross-section SEM images show that a selective sidewall erosion occurs since some III-V etching subproducts are more volatile than others. Increasing the H_2 flow enhances the atomic chlorine scavenging in the plasma which decreases the chemical etching. FIB-STEM characterizations show that no sidewall erosion is obtained when a high H_2 flow is used (67%). TEM-EDX measurements show that a 50nm-thick SiO_xCl_y layer is deposited on the sidewall which helps limiting the sidewall erosion and ensure anisotropic etching. ToF-SIMS measurements show that hydrogen atoms were incorporated into the III-V/Ge sidewall and its concentration increases with the H_2 flow. Cathodoluminescence measurements were performed on the etched sidewall as well. In the vicinity of the top sub-cell, the etched sidewall presents a higher luminescence intensity and it is even larger with increasing H_2 flow. These results show that adding H_2 to the plasma mixture allows hydrogen incorporation into the sidewall which passivates the non-radiative defects. As a result, both the open-circuit voltage and the fill factor of the solar cell are higher with increasing H_2 flow, resulting in a higher cell efficiency.

PS-Contributed On Demand-118 Process-induced Damage in GST Etch*, Luxherta Buzi,* *J. Papalia, H. Miyazoe,* IBM*; H. Cheng,* Macronix International Co*; M. Hopstaken, R. Bruce, S. Engelmann,* IBM

As the semiconductor industry continues to push for and develop higher performance computing systems, there is also a growing trend of developing new computing approaches to be more energy efficient. 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. These PCM materials (e.g., GeSbTe and its derivatives) can be damaged during plasma etch processing leading to defects such as void formation, grain coarsening, selective material depletion, etc. In addition, the etch damage of PCM materials can affect device performance (e.g., switching times). Optimization of etch process and chemistry in minimizing or eliminating structural or compositional damage is crucial for success of this new device technology.

Experiments were performed on thin GST films to reveal the effects of chemistry and the impact of different plasma configurations on recrystallization properties and damage formation. No significant difference in damage formation was found for different reactor configurations in Ar plasma (ICP, MW, IBE), however the effect of UV/VUV irradiation and other chemistry effects have to be more extensively studied with alternative reactor configurations. Using halogen chemistries, enhanced damage was observed for different reactor configurations (ICP vs. MW). Here, the depth profiling analysis showed a correlation between the enhanced damage formation and selective elemental depletion and plasma residue retention in the near surface region.Chlorine plasma had the highest etch rate and increased damage formation compared to HBr and CF_4.

PS-Contributed On Demand-121 Double Curling Probe Method for in-situ Monitoring of Electron Density and Film Thickness for Application*, Daisuke Ogawa,* *H. Sugai, K. Nakamura,* Chubu University, Japan

Knowing plasma parameters, such as electron density and temperature etc., is a key to increase reproducibility in material processing. There are numerous techniques to measure these parameters, along with their advantages and disadvantages. The numerous techniques are necessary because it is always a good idea to make these parameters crosschecked with other techniques to increase the reliability of the values.Curling probe is one of the diagnostic tools that utilizes resonance in microwave range with a curl-shaped slot antenna.The probe deals with the plasma as a dielectric material.The probe enables the measurement of the electron density in plasma from the shift of the resonant frequency: the degree of the shift depends on the electron density. However, material processing sometimes requires a film deposition, which affects the measurement with the probe. The deposited film can be a dielectric material so that the film lets the frequency shift as well.It means that such a deposition process allows shifting the frequency both due to plasma and due to film deposition.Therefore, a curling probe can be available in a situation where the effect of film deposition is neglectable.

To overcome the measurement of electron density in the situation where film deposits, we have recently developed the technique with the use of two curling probes (D. Ogawa et al., PSST, accepted on Feb. 2020).This technique allows separating the summation of the frequency shifts with the use of the probe character, where a frequency shift is dependent on the probe diameter.Our preliminary result shows that the new technique successfully derives the electron density and film thickness at the same time.However, note that we obtained this result in a simulated situation when the generation of the plasma was with argon gas, and the deposited film was as polyimide tape.This result was good enough for the preliminary data and to practically prove the theoretical approach, but it is still far from an application in actual processing.It means that there are still some works that need to get done, for example, measurement with a complex gas, and even with a reactive gas used for depositions.In this presentation, we will report some updates on this technique for application in the production line.

PS-Contributed On Demand-124 Low Energy, High Flux Density Ion Assisted E-Beam Evaporation Using a Tunable and Robust Rf Plasma Ion Source*, M. Reilly, R. Viswan,* ***David Douglass,*** Denton Vacuum, LLC

Ion assisted deposition (IAD) using e-ebeam evaporation is a well-known deposition method commonly used for optical films. One of the advantages is moisture stability of the films' optical properties.However, many materials are not suitable for IAD as the typical ion sources used provide either a high flux of energetic ions above the material dissociation energy, or a low flux of low energy ions insufficient to densify the optical films.

Denton Vacuum's patented Endeavour RF plasma ion source has the capability for independent control of ion current density and ion energies over a wide range. The ion current density can be controlled by the RF power applied to the RF coil, and the ion energies can be controlled using a DC voltage applied to an electrode, biased positively with respect to a grounded single grid. This combination enables a high flux of ions with tunable ion energy.We demonstrate this tunability in both moisture shift control and stress tunability. Moisture shift in HfO$_2$, Al$_2$O$_3$, and SiO$_2$ thin films with no ion-assisted deposition was 0.95%, 0.23% and 0.47% respectively. By varying the ion energies from about 50 eV to 300 eV, the moisture shift could be reduced to 0.19%, 0.17% and 0.04% for HfO$_2$, Al$_2$O$_3$, and SiO$_2$ respectively. Intermediate moisture shifts were obtained at lower ion energies, indicating that the source is suitable for applications demanding low energy/high flux ion assisted deposition (IAD).

In addition, the stress could be tuned for example, in Al$_2$O$_3$ films from 29 MPa (tensile) to 2.23 MPa (compressive) by increasing the ion energy from 0 eV to about 100 eV. More importantly, since the ion energy and ion flux can be independently controlled, the source can be operated at low ion energies with a high ion flux and in regimes not accessible to most standard ion sources used for IAD. This ion source is also robust and requires very low maintenance and is suitable for a variety of applications such as ion beam deposition, as well as for pre-clean and etching.

PS-Contributed On Demand-127 Etch Behavior of Post-Copper Metals*,* ***John Arnold,*** IBM Research Division, Albany, NY*; N. Joy,* TEL Technology Center, America, LLC*; H. Miyazoe,* IBM Research Division, T.J. Watson Research Center*; C. Park, A. Simon,* IBM Research Division, Albany, NY*; C. Cabral, H. Yan, F. Stellari,* IBM Research Division, T.J. Watson Research Center*; S. Rogalskyj,* TEL Technology Center, America, LLC*; E. Richardson,* TEL Technology Center of America*; A. Raley,* TEL Technology Center, America, LLC*; S. Engelmann,* IBM Research Division, T.J. Watson Research Center

For more than two decades and through approximately ten technology nodes, the semiconductor industry has relied upon dual Damascene copper interconnects.While there is vigorous debate as to the timing and dimensions of the transition, it has become clear that there will eventually be a need to replace copper with a different conductor metal. Motivations include copper's requirement for space-consuming diffusion barriers and the contributions of interfacial electron scattering to higher resistance at smaller dimensions. Researchers such as D. Gall[1] have proposed a range of candidate conductor metals, generally with a focus on the projected scaling behavior (i.e., resistance vs dimension) of ideal materials.

In this study, we examine the practical implications of conductor metal selection and the metal's processing, with a specific focus on those metals which are able and likely to be patterned by subtractive methods. For example, it is recognized that lower sheet film resistivity is generally favored by deposition or annealing processes which result in larger grains within the metal film, but the effect of grain size on parameters such as Line Edge Roughness (LER) and line height variation must be taken into consideration. Additionally, a material's ability to withstand downstream processing and our ability to etch it with the desired profile may influence its competitiveness as a copper replacement. We will explore the interactions of material choice, deposition technique, seed layers, annealing, etch processes, and downstream processing on final interconnect performance.

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PS-Contributed On Demand-130 Radical Flux Control using a Dual Exhaust System during Reactive Ion Beam Etching (RIBE) Process*,* ***Doo San Kim****, Y. Jang, Y. Kim, H. Gil, G. Yeom,* Sungkyunkwan University, Korea (Republic of)

The radicals generated during the reactive ion etching (RIE) process are electrically uncontrollable and cause isotropic etching and chemical damage to the etched pattern sidewalls. For this reason, precise etching control is difficult in a nanoscale pattern of 10 nm or less, and there is a problem of deterioration of device characteristics due to chemical damage. In this study, a reactive ion beam etching (RIBE) system was used to study the effect of relative fluxes of reactive ions and radicals reaching the substrate during RIE processes. To control the relative flux between ions and radicals to the substrate, a dual exhaust system is introduced into the RIBE system to control the amount of radicals generated in the plasma. It is used to control the flux of radicals and ions to the substrate during the RIE process using CF$_4$ gas. The results showed that the additional exhausting of the radicals through the ICP source chamber not only decreased the ICP source chamber pressure but also decreased the ratio of radical flux to ion flux to the substrate. Therefore, the fine pattern etched with the RIBE system with the dual exhaust system reduced the sidewall etch of the pattern by radical reduction.

PS-Contributed On Demand-133 Inactivation of Human Coronavirus in Circulating Air Flows Using a Multielectrode Dbd Setup*, A. Demaude,* ***Delphine Merche****, D. Petitjean, M. Depessemier, E. Silberberg, A. Op De Beeck, F. Reniers,* Université libre de Bruxelles, Belgium

The COVID pandemic stimulated research aiming at reducing viruses transmission between humans. Medical data, as well as modelling revealed that transmission is highly increased in interior of buildings. To reduce viruses concentrations in the air, many tools have been proposed, some of them showing an efficiency. In this paper, we designed a model multielectrode DBD dedicated to be placed in tubing systems used for air circulation or recycling. The gap between the electrodes was calculated to allow lighting up the plasma in air at moderate voltages. The whole DBD setup was placed in a closed container allowing to collect remaining virus particles.

A spray system able to inject continuous amounts of microdroplets in air was placed on top of the DBD setup. The whole setup was place in a dedicated hood, with a safety level of 2.

Solutions containing HuCOV229E viruses (human coronavirus 229E) were then sprayed in the middle of the DBD setup.

Variable injection speeds were tested in the range of a few hundred µl/min. An air DBD plasma was lighted using a AFS sinusoidal generator operating at 29.4 kHz with our without pulsing. The treatment time was fixed at 90 sec (spray time and plasma time). The plasma power was varied between 20 and 50 W. Careful control of the reactor and electrode temperature was performed in order to avoid that the virus inactivation was due to temperature effects. The viral solution was collected downstream.

After the treatment, the reactor and the electrodes were rinsed to collect possible virus remaining and this was added to the main collected sample.The collected viral solution was then titrated to determine the remaining viral activity on cells. Every experiment was replicated 3 times. A significant decrease of viral activity (Log 2 decrease) was obtained in specific conditions. Future possibilities and development of such setup will be discussed.

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PS-Contributed On Demand-136 Insertion Characteristics of Plasma Nitrided Suture Needle in Long Incision*,* ***Takao Yamauchi,*** Meijo University Graduate School, Japan*; P. Abraha,* Meijo University, Japan

Austenitic stainless steels are biocompatible materials that have high corrosion resistance, suitable for suture needles. The austenitic stainless steel material, on the other hand, has a lower hardness that makes it difficult to maintain the sharpness of the needle tip and secure the shape of the suture needle resulting in a shorter life span. In this study, we performed plasma nitriding treatment, a hardening process, to strengthen the stainless steel surgical suture needles and suppress needle deformation in long incisions.

In recent years, various researchers have suggested ideas on maintaining the sharpness and improving the durability by coating suture needles with silicone. Others have indicated reducing insertion force by improving friction characteristics with metallic glass coating. However, coating the needles changes the sharpness of the needle tip, and risks peeling off during use.

In this experiment, low-energy plasma was used to treat the suture needles to maintain the surface roughness by suppressing the edge effect.Moreover, the diffusion-based hardening method was used to secure the shape, and avoid dimensional changes and the danger of delamination. Here, suture needles with different nitrided layer thicknesses were used to evaluate the insertion characteristics in long incisions. The results show that the deformation of the plasma nitrided suture needles was reduced to one-third that of the untreated needle after 30 sutures. In this presentation, we will show the results of the performance of the suture needles treated by our biocompatible plasma nitriding system.

PS-Contributed On Demand-139 Investigation of CHM Etching with Additive Gas*, Kathryn Maier*, *L. Kovatch, Y. Ishii,* Hitachi High Technologies America Inc.

Over the many years of device scaling, integration has become more and more complicated. As a consequence, the number of etching processes as well as other manufacturing steps have increased tremendously. Hard-mask (HM) structure, which consists of photoresist mask/SiO-like layer/carbon-hard mask (CHM)[1], is one of the structures frequently used for patterning. In order to successfully transfer the HM pattern into the following layer, understanding the etching behavior of CHM is a critical factor, especially for CHM etching characteristics and their interactions with other films in relation to the etched profile.

In this investigation, we evaluated the temperature behavior of the CHM etch with some gas addition. We found that etch rate decreases with increasing temperature. This etch rate trend can be changed with or without the additive gas. It is found that oxide layer formation plays an important role in the behavior, which may or may not be observed depending on the temperature, even with the additive gas included in the process. We will reveal the correlation between the temperature and the gas flow during the presentation, with the support of surface analysis.

During the CHM etch, selectivity against upper or underneath layer, such as SiO-like or SiN-like layer, needs to be taken into account so as to etch CHM vertically. The use of the additive gas is utilized to obtain the high selectivity. In this presentation, we also analyzed the selectivity mechanism against oxide and nitride. The analysis shows that oxide layer formation on the oxide and nitride enhances the selectivity. It is shown that the oxide layer is slightly different from SiO2 layer, which is confirmed by surface analysis.

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PS-Contributed On Demand-142 Effect of Synchronously and Asynchronously Pulsed Ar/Cl_2 Inductively Coupled Plasmas on Si Trench Formation*, Heeju Kim*, *G. Yeom, L. Wen, j. hong, W. Jang, S. Namgoong,* Sungkyunkwan University (SKKU), Korea (Republic of)

Traditionally, continuous wave (CW) plasma etching has been used for the fabrication of semiconductor devices. However, due to the several issues such as plasma induced damage (PID), charging issues, aspect ratio dependent etching (ARDE), etc., pulsed plasma etching technologies are applied and getting more attention for nano-scale device fabrications to solve problems of conventional CW plasma etch processes.

In this work, we investigated the nanometer scale poly Si trench etch processing using variously pulsed Ar / Cl_2 inductively coupled plasmas such as synchronized pulsing, asynchronous pulsing, etc. The differences in the etching characteristics and plasma characteristics of CW, synchronous, and asynchronous ICP plasmas have been investigated. It has been found that, compared to CW plasmas, synchronously pulsed plasmas showed better etch profiles and lower ARDE effect. Especially, the further decrease of ARDE effect was observed with asynchronously pulsed plasmas compared to synchronously pulsed plasmas even though the etch rate has been decreased. To understand the mechanism of etch etching by variously pulsed plasmas, plasmas have been characterized with high voltage probes, time resolved OES, RGA, etc. Also, the XPS measurement has been performed to understand chemical reactions on the etched material surfaces.

PS-Contributed On Demand-145 Two-Dimensional Particle-in-Cell Simulation for Spatial Nonuniformity of Ion Energy and Angle Distributions in Dual-Frequency Capacitively Coupled Ar Plasmas*, Ji Hyun Shin*, *C. Kim, G. Park, H. Kim, H. Lee,* Pusan National University, Korea (Republic of)

Dual-frequency (DF) capacitively coupled plasmas (CCP) are commonly utilized in semiconductor etching and deposition processing because of their excellent spatial uniformity and easy control of ion energy. With a dual-frequency, the ion energy and the ion flux are separately controllable for the high-frequency (HF) and the low-frequency (LF) voltage waveforms, which are faster and slower than the ion transit time individually. A two-dimensional particle-in-cell simulation parallelized with a graphics processing unit made it possible to overcome the heavy computation load in DF CCP simulation. In this presentation, we report the asymmetry electrode effect on the spatial uniformity of the ion energy and angle distributions of Ar CCPs under DF driving conditions. The plasma potential and the ratio of the ion power loss to the electron power loss increases with LF power. Despite the spatial nonuniformity of plasma density, the ion flux toward the wafer is uniform when the upper electrode is longer than the lower electrode beneath the wafer. However, time-dependent analysis of ion energy and angle distributions (IEADFs) shows that nonuniformity still exists for the angle distributions.

PS-Contributed On Demand-148 Plasma Induced Disproportionation of Nitrogen in a DC Plasma-Electrolysis System Operated in N2 at Atmospheric Pressure, *C. Pattyn,* Université libre de Bruxelles, Belgium, France*;* ***Nicolas Maira,*** Université libre de Bruxelles, Belgium, Italy*; A. Remy, F. Reniers,* Université libre de Bruxelles, Belgium

Since the beginning of the twentieth century, the Haber-Bosch process has been used for the fixation of nitrogen through the synthesis of NH_3, an essential precursor for the production of fertilizers. However, despite being extensively optimised, it accounts for more than 1% of global carbon dioxide emission and the global energy consumption [1]. Furthermore, its dependence on hydrocarbon precursors (mainly from fossil origins) for the production of H_2 via steam reforming highly compromises its future involvement in a sustainable society [2]. Over the past few years, plasma-based processes have attracted more attention as a “clean” alternative to Haber-Bosch for nitrogen fixation. This is due to the unique properties of non-equilibrium plasmas which could allow a drastic reduction of the energy cost for nitrogen fixation while being compatible with renewable precursors and energy sources.

In this study, a DC plasma-electrolysis system is used for the simultaneous oxidation (NO_x) and reduction (NH_3) of nitrogen, using a setup that has already demonstrated a significant interest for the selective synthesis of NO_3^- [3]. The discharge, ignited in pure N_2 between a stainless steel needle and the solution (1mM of NaCl) is used as a cathode electrode while a platinum wire immersed in the liquid of is used as an anode electrode. The solution is analyzed by means of ionic chromatography and UV-Vis spectrophotometry while the plasma/gas phase is analyzed using optical emission spectroscopy and electrochemical sensors.

Experiments highlight that ammonia is formed mainly in the gas phase through multiple pathways which benefit from hydrogen evolution reaction at the plasma-liquid interface. Interestingly, lowering the plasma-electrolysis current down to 1mA proved to allow the reduction of the energy cost for nitrogen fixation (down to 61.1MJ/mol) while enhancing the transfer of nitrogen compounds from the gas phase to the liquid phase (in the form of stable secondary species such as NO_2^-, NO_3^- or NH_4^+). This results from both an enhancement of the non-equilibrium properties of the discharge, allowing a higher vibrational excitation of N_2, and a more efficient conversion of nitrogen compounds to species with a higher solubility (in particular regarding the oxidation of nitrogen). The (artificial) enhancement of the water vapor content in the gas mixtures has lead to further improvement of the vibrational excitation of N_2 and lowering of the energy cost while preserving a somewhat similar selectivity of the nitrogen compounds produced.

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PS-Contributed On Demand-151 The Role of Plasma Properties in Plasma Enhanced Atomic Layer Epitaxy*, Scott Walton*, *D. Boris, V. Wheeler, N. Nepal,* Naval Research Laboratory*; S. Rosenberg, J. Avila, J. Woodward, V. Anderson,* ASEE*; C. Eddy, Jr.,* 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. The advantages come at the cost of a complex array of process variables that often require great care on the part of the user. 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 a commercial PE-ALD tool (Fiji 200; Ultratech/CNT). 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 employed to grow nitride and oxide films. Changes in plasma parameters are then linked with changes in the 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.

PS-Contributed On Demand-154 Area Selective Plasma Enhanced Chemical Vapor Deposition of Silicon Using a Fluorinated Precursor*, **Ghewa Akiki,*** LPICM-CNRS, Ecole Polytechnique, Institut Polytechnique de Paris, France*; S. Filonovich,* TOTAL GRP, France*; M. Bouttemy, M. Fregnaux,* Institut Lavoisier de Versailles, UMR CNRS 8180, Université de Versailles-St-Quentin, France*; I. Florea, P. Bulkin, E. Johnson,* LPICM-CNRS, Ecole Polytechnique, Institut Polytechnique de Paris, France

Area-selective deposition(ASD) is a process that controls where the deposition takes place through the underlying surface rather than through any masking step. This can be achieved by either Atomic Layer Deposition (ALD) or Chemical Vapor Deposition (CVD) techniques [1]. In previous work, we studied area selective plasma enhanced CVD (PECVD) using an $Ar/SiF_4/H_2$ plasma chemistry [2]. For specific plasma parameters, a microcrystalline silicon film is selectively grown on a SiO_xN_y area while the AlO_x adjacent area remains pristine (see figure 1). This effect was then attributed to the formation of Al-F bonds that blocks the deposition of silicon on top of the AlO_x area [3].

However, when the plasma conditions are changed or when those two materials are patterned using lithography, the selectivity is lost. Each case will be discussed and presented based on in-situ ellipsometry and X-ray photoelectron spectroscopy analyses.

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PS-Contributed On Demand-157 Driving Frequency and Ozone as Key Parameters for Nitrogen Oxidation by a Dielectric Barrier Discharge in an N_2-O_2 Mixture*, **Antoine Remy,*** Université libre de Bruxelles, Belgium*; N. De Geyter,* Ghent University, Belgium*; F. Reniers,* Université libre de Bruxelles, Belgium

Dielectric barrier discharges (DBDs) have a wide field of applications, ranging from coating depositions [1] to gas conversions [2]. The addition of nitrogen to oxygen in ozonisers allows a better ozone (O_3) yield due to reactions with nitrogen species. But at some point, the nitrogen added will limit the ozone output because of nitric oxide (NO) poisoning [3]. Therefore, in O_3 production from air, the side production of nitrogen oxides (NO_x) in various forms has always been seen as a pollutant. For nitrogen fixation by oxidation, we created a discharge into nitrogen and oxygen while optimizing the NO_x output over frequency, power and oxygen ratio. Nitric oxide is known to be efficiently produced at high temperature due to the reaction between vibrationally exited N_2 and atomic oxygen [4], unlike O_3 which is best produced at low temperature [3]. By adjusting the parameters, we can find the perfect balance between NO and O_3 production that allows to use O_3 as an oxidizing agent for NO and thus locking NO_x species in higher oxidation states (HNO_3, NO_2, N_2O_5). The hydrogen needed is coming from the polymer walls of the reactor or remaining water. The reactor is a plate-to-plate DBD with two dielectrics (3 mm quartz) separated by a 2 mm gap, in a continuous flow rate (0,5 to 6 L/min) of an N_2/O_2 gas mixture (10% to 90% of oxygen). The total flow rate of the reactor and the oxygen concentration has been studied over four driving frequencies (4 kHz, 12 kHz, 17 kHz and 30 kHz) to optimise the energy efficiency (ppm/W.s) of NO_x. In-situ Fourier transform infrared spectrometry has been used to monitor nitrogen oxides production as function of discharge time. It allowed us to follow the concentration in the reactor of O_3 and NO_x from 0 to 250 s of discharge time with a 1 second resolution. The concentration evolution and energy efficiency using different frequencies show three different behaviours of NO_x and O_3 production in the discharge. Among them, 17 kHz shows the highest energy efficiency at 50% oxygen concentration and a flow rate of 1 L/min mainly through the production of HNO_3. At 6 L/min, 30 and 17 kHz frequencies tend to have both the highest energy efficiency whereas the lower frequencies (4 and 12 kHz) mainly produce NO and NO_2 at all flow rates and oxygen concentrations under study and at lower energy efficiency. We thus emphasize here the correlation between ozone and nitrogen oxides production and the influence of the driving frequency.

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PS-Contributed On Demand-160 Are Atmospheric Plasmas Environmental Friendly? A Case Study*, R. De Cruyenaere,* Université libre de Bruxelles, Belgium*; N. Vandencasteele,* CPI Plasma, France*; W. Achten,* ***Francois Reniers,*** Université libre de Bruxelles, Belgium

Plasma technology, and more specifically atmospheric plasma, are often referred as green technologies. Indeed,they do not use (toxic) organic solvents, they operate at atmospheric pressure, therefore without the need of pumping systems, they use electricity that can be produced by green technologies, and they are most often "cold" plasmas, meaning that the energy loss in heating the gas is limited. These arguments are often used either in conferences, or by manufacturers of equipment to justify the choice of the technology. However, there are limited scientific data showing the real environmental impact of (cold) atmospheric plasma [1]. Through a case study, the environmental impact and the eco-efficiency of plasma treatments are calculated and compared with their traditional counterparts. The environmental impact, through the life cycle analysis (LCA) is calculated using the SimaPro software and the EcoInvent database.

Surface activation of polymers to increase their surface energy and their adhesion properties is one of the major uses of cold atmospheric plasmas (such as dialectric barrier discharges -DBDs). In this study, surface activation of a model polymer using a high speed atmospheric dielectric barrier discharge operating in a nitrogen atmosphere is compared to a traditional wet chemistry surface activation. Both processes present advantages and drawbacks. A DBD necessitates high gas flows and, for nitrogen used as a gas, a very high voltage, but do not produce significant residues. The wet chemistry approach requires aggressive chemicals, diluted possibly in water. Heating is required to evaporate the solvent, whereas chemical residues have to be collected. On the other hand, it does not require advanced plasma technology.

After having defined the perimeter (the limits) of the analysis, the impact of the energy injected in both treatments, the environmental cost of the reactants and of the release of the byproducts has been evaluated.

A global eco-efficiency of both treatments is established and discussed and the limits of the LCA model are discussed for this specific case study. Extension to other plasma processes is discussed

Reference :

[1]. Anastasopoulou, et al. A., *Industrial & Engineering Chemistry Research*,(2016) *55*(29), 8141–8153. https://doi.org/10.1021/acs.iecr.6b00145

PS-Contributed On Demand-163 Spatio-Temporal Characterization of a Pulsed DC Atmospheric Pressure Plasma Jet Interacting With Substrates*, **Michael Johnson,*** National Research Council*; D. Boris, T. Petrova, S. Walton,* Naval Research Laboratory, USA

Atmospheric pressure plasma jets (APPJs) generate an environment with unique electrical and chemical properties in the open air, making them attractive for a variety of surface treatment applications. The broad operational space of APPJs allow for the treatment of metal, ceramic, plastic and biomaterial surfaces. When a plasma contacts a surface, the electrical and chemical characteristics of the entire plasma jet can change based on the properties of the surface. This interdependency between the plasma and the surface during plasma-surface interactions creates a complex system, where changes to one will result in changes to the other. Understanding the plasma-surface interactions and the associated changes to plasma properties thus becomes critical in advancing the use of APPJs to treat surfaces. In this work, the evolution of a pulsed-DC APPJ, produce in a helium flow and contacting different surfaces is studied using temporally- and spatially-resolved optical emission spectroscopy. Gold and glass substrates are used as exemplary conducting and insulating substrates.On an insulative surface, a surface ionization wave forms which briefly spreads out across the surface. With a conducting substrate, a series of different features form on the surface that will last the entire duration of the voltage pulse. Emission associated with select species, such as helium, nitrogen and hydroxide, are investigated to understand the kinetics within the plasma. Different ratios between emission lines are determined to understand the relative contribution of electrons and metastable states in driving species production during the active and afterglow phases of plasma generation. This work is supported by the Naval Research Laboratory base program.

PS-Contributed On Demand-166 Modulation of Synergy in Metal ALE: Film Composition Effects*, **Nathan Marchack**, E. David, D. Kazem, B. To, M. Hopstaken, S. Engelmann,* IBM Research Division, T.J. Watson Research Center

Titanium Nitride (TiN) is a well-established material in CMOS fabrication, and has recently continued to fulfill hard mask and electrode roles in novel technologies such as carbon-based dopamine sensors[1] and RRAM.[2] However, the material's inherent physical properties, particularly its low surface binding energy, make it a poor candidate for plasma-enhanced atomic layer etching (ALE) techniques, where spontaneous etching can be observed even at zero bias conditions.[3]Thermal ALE approaches involving surface oxide conversion followed by removal using a fluorine-based chemistry have been demonstrated,[4] however, temperature constraints in integration schemes diminish the utility of these approaches.

We demonstrate how surface modification of TiN in an inductively coupled plasma (ICP) discharge using O_2 and H_2 chemistries can be used to modulate etch selectivity to the bulk TiN material in F- and Cl-based plasmas, respectively. For the case of surface oxidation, bias power was the most impactful knob in inducing comparable results to thermal approaches (~250C), as measured by x-ray photoelectron spectroscopy. The variation in film properties, particularly local oxygen concentrations, induced by the physical vapor deposition (PVD) method and its subsequent effect on etch processes were also studied. Excellent across wafer uniformity is demonstrated with this approach over continuous-wave (CW) plasma processes.

For H_2 plasma exposure, pressure was found to be the most significant control in modulating etch resistance, with a process window for sub-nm ER/cycle found at 50 mTorr (see suppl. doc.). V_{DC} measurements from the ICP reactor were largely uncorrelated to the etch rate modulation. The effect of this treatment of a Si surface was investigated for integration schemes requiring tailored selectivity.

[1] Engelmann, Ando and Narayanan, AVS 66th Symposium, Columbus, OH (2019)

[2] Demuru, Nela, Marchack et al, ACS Sensors 3, 799 (2018)

[3] Marchack, Papalia, Engelmann and Joseph, JVSTA 35, 053C14 (2017)

[4] Lee and George, Chem. Mater. 29, 8202-8210 (2017)

PS-Contributed On Demand-169 Bridging the Gap Between Plasma Spectroscopy and Catalytic Analysis: A Study on CO_2 Methanation*, **Lucas Quintana**, E. Fisher,* Colorado State University

Plasma-assisted catalysis (PAC) is a process that has been investigated as a promising solution to combat increasing environmental concerns. To remain a viable option for pollution control, however, a thorough understanding of the underlying synergisms between the catalyst and plasma must be elucidated. In this work, optical emission spectroscopy was employed to assess the impact of zeolite and Ni/zeolite catalysts on relative species densities and energy partitioning trends in H_2 and mixed gas H_2/CO_2 inductively coupled plasma systems. In a 90:10 H_2:Ar plasma, where Ar is used as an actinometer, H_2 rotational temperature (T_{rot}) was ~500 K regardless of the presence of a catalyst. In the 1:1 CO_2/H_2 mixture in the presence of a catalyst, T_{rot} nearly doubled to a range of 1000-1200 K. Thus, some underlying synergy exists between all the components in the plasma system. Possible changes to the catalyst as a result of exposure to the plasma were examined using scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS) and with powder x-ray diffraction (pXRD). Catalyst analysis by SEM-EDS and pXRD revealed that the morphology and bulk chemical characteristics of the catalyst remained largely unchanged after exposure to plasma, indicating that these catalysts are robust and reusable in a PAC system. Collectively, these data provide insight into the fundamental plasma interactions in PAC systems, which will ultimately lead to deeper understanding of the ever-growing atmospheric pollution problem. In addition, this work sets the stage for future work examining the methanation of CO_2 utilizing plasma technologies.

PS-Contributed On Demand-172 A Low-Cost Atmospheric Pressure Plasma Apparatus to Depyrogenate Delicate Materials in a Sealed Environment*, **Naman Bhatt**, D. Trosan,* North Carolina State University*; J. Brier-Jones,* Loma Linda University, Karamedica, Inc.*; J. Pecoraro,* North Carolina State University*; J. Smallwood,* Loma Linda University*; A. Crofton,* Case Western Reserve University, Karamedica Inc.*; S. Hudson,* North Carolina State University, Karamedica*; W. Kirsch,* Loma Linda University, Karamedica, Inc.*; K. Stapelmann, S. Shannon,* North Carolina State University

One of the biggest challenges in the pharmaceutical industry is to produce low-cost pyrogen-free material that can be used in internal medicine. Chitosan is one such material that has shown promising results as a drug carrier in targeted treatments of cancer and Alzheimer's disease. Chitosan is currently being evaluated by our collaborators as a potential key component of a prophylactic treatment for COVID-19 (coronavirus). An efficient and cost-effective depyrogenation process with validation of endotoxin reduction can be of huge benefit to the medical industry.

Pyrogens, such as endotoxins, are ubiquitous and can easily be attracted from non-sterile environments. Endotoxins cause an inflammatory response in the human body and a significant amount can cause an endotoxic shock with high fever, organ failure, and even death. Endotoxin is notoriously difficult to destroy or inactivate as it is highly stable in temperature and pH changes and varies in size and molecular weight. In addition, endotoxins have strong binding affinity for chitosan molecules. Conventional sterilization processes including dry or wet heat, radiation, and chemical sterilant cause alterations to chitosan's properties and may leave toxic residues.

In this talk, we present a low-cost high-volume atmospheric pressure plasma apparatus that allows controlled plasma processing in a sealed environment. A dielectric barrier discharge is built to perform depyrogenation inside hermetically sealed bags. Design challenges and considerations are discussed. FDA requires at least a 3-log reduction in endotoxin levels for depyrogenation processes. However, there is not any quantified data in literature for endotoxin reduction using plasmas. We carried out a detailed experimental study with plasmas of different gas mixtures including synthetic air, nitrogen, and helium and were able to achieve up to a 4-log reduction in endotoxin levels. FTIR and Raman spectroscopy measurements revealed no structural change in chitosan after the plasma process. Surface modifications of different bag materials are also presented through FTIR and Raman spectroscopy.

This work is supported through the NIH SBIR program and Karamedica, Inc.

PS-Contributed On Demand-175 Two-Dimensional Inductive Coupled Plasma Remote Source Modeling and Experimental Validation With Different Gas Mixtures*, **Abhra Roy**,* ESI Group*; L. Zhang, Y. Yang, S. Ma,* Mattson Technology, Inc.

2D axisymmetric numerical model has been developed to simulate an inductive coupled plasma (ICP) discharge in plasma reactors with remote source for resist ashing and surface treatment applications. Commercial modeling software, CFD-ACE+ was used for simulations of inductively coupled plasma reactor (without wafer bias) to address gas flow, heat transfer, plasma chemistry and electromagnetics in a coupled fashion. Maxwellian EEDF, quasi-neutrality of electron/ion density balance, and ambipolar electric field is assumed. Several gas phase and surface chemistries are developed on pure and mixtures of gases, we will address discharge of Argon, Nitrogen, Helium, Oxygen and N2/O2 mixture. Initially, the fast global (0D) model has been used to help isolate the major reaction pathways and enable reduction of the large volumetric mechanisms used in multidimensional simulations. Then the models are applied to simulate 2D reactor for all the gas discharges. Model predictions of plasma, ion and important active species densities, and electron temperature are reported. Experimental measurements are performed in Mattson's Suprema Asher, a downstream ICP reactor with patterned grounded Faraday shield [1] to reduce electron temperature and ion energy, as well as charge separation conductive grid between the plasma source and heated pedestal to reduce ion concentration on the wafer surface. Retractable Langmuir probe is inserted into plasma source through the special top cap with three openings, defining the vertical axes along which plasma density and electron temperature are repeatedly measured. Both numerical and experimental data are presented in a comparative manner. Model calibration has been performed based on experimental data, primarily modifying the gas phase reaction steps (reaction rates. collision cross section data) in several stages. Using the final model, a close match of result is observed lading a proper validation. This numerical model has been further used to simulate parametric process recipes.

[1] Stephen E. Savas, Brad S. Mattson, Martin L. Hammond, Steven C. Selbrede, Patent US 6143129.

PS-Contributed On Demand-178 Etching Characteristics of Low-K SiCOH Thin Films Deposited by Plasma Enhanced Chemical Vapor Deposition Using Tetrakis(Trimethylsilyoxy)Silane Precursor*, **Jacob Comeaux**, W. Wirth, S. Jang,* University of Louisiana at Lafayette

As semiconductor devices get smaller, one issue that arises is the resistance-capacitance (RC) delay in the interconnects, resulting in the degradation in the performance of devices. To reduce the RC delay, the dielectric constant can be reduced by using a low-k dielectric (k<4.0) in place of traditional SiO_2 (k=4.2) for the intermetal dielectric (IMD) material. The interconnects integration requires the dielectric patterning followed by metal filling, so-called “Damascene” process. This brought the need for low-k dielectric patterning by plasma etching. There are some challenges in etching of low-k materials due to their low density and porous structure. In this study, the effect of plasma etching on the low-k properties was demonstrated. The low-k SiCOH thin films were deposited on silicon (Si) wafers using plasma enhanced chemical vapor deposition (PECVD) of the precursor tetrakis(trimethylsilyloxy)silane (TTMSS). The deposition conditions varied the RF plasma power from 20 to 100 W, and the process pressure from 26.7 to 66.7 Pa. The deposited films then underwent a reactive ion etching (RIE) in CF_4, O_2, and Ar at varying etching conditions including the flow ratios, pressure, and RF power. Characterization of the films was performed before and after RIE. Chemical characterization was performed by Fourier transform infrared (FTIR) spectroscopy and X-ray photoelectron spectroscopy (XPS). The composition of thin films affected the reaction between etching gases and the film surface. CF_4 gas contributed to the volatile Si compounds such as SiF_x. By adding O_2 to CF_4, carbon materials can be removed by forming CO and CO_2. The concentration of F-radicals in the plasma determined the etch rate. The etching chemistry strongly depended on the structure and composition of SiCOH films. In addition to the change in the chemical structure of SiCOH films after RIE, material properties of as-deposited SiCOH films were compared with those of etched films: mechanical properties including elastic modulus and hardness measured by nanoindentation, refractive index and film thickness (deposition rate and etch rate) using ellipsometer, surface morphology observed by atomic force microscopy (AFM), and electrical properties including dielectric constant and leakage currents measured with capacitance-voltage (C-V) and current-voltage (I-V) curves.

PS-Contributed On Demand-181 Enhancing the Far Ultra-Violet Optical Properties of Aluminum Mirrors with a Plasma Based Approach to Oxide Removal and Fluorine Passivation*, **David Boris,*** U. S. Naval Research Laboratory*; L. Rodriguez de Marcos,* Catholic University of America*; A. Kozen, S. Rosenberg,* ASEE Postdoctoral Fellow*; J. del Hoyo, J. Richardson, E. Wollack, M. Quijada,* NASA Goddard Space Flight Center*; S. Walton,* U. S. Naval Research Laboratory

Astronomical instrumentation/telescopes operating in the Far Ultra-Violet (FUV, 90-200nm) require the use of aluminum mirrors due to its high reflectivity over this wavelength range.Unfortunately, the native aluminum oxide layer formed in atmosphere is strongly absorbing in this wavelength range, requiring that the aluminum films be passivated with a dielectric/transparent layer that inhibits oxidation.Efficient optics in the FUV range are challenging due to the limited selection of protective transparent materials available for use on aluminum. A promising coating materials is AlF_3, which can protect the underlying aluminum and yields a theoretical reflectivity of » 50% down to 100 nm, if the coating is sufficiently thin.In this work, we explore the use of electron beam generated plasmas produced in an SF_6 background to simultaneously remove the native oxide layer, while depositing an AlF_3 capping layer to passivate the aluminum.XPS measurements indicate that this approach is capable of producing thin (15 - 30 nm) AlF_3 films with some mild ($\leq$5%) oxygen contamination. We will discuss the impact of plasma power, plasma chemistry, and plasma exposure time on the composition and structure of the passivation layer and how those parameters affect the optical properties. This work is partially supported by the Office of Naval Research, the Naval Research Laboratory base program, and NASA Strategic Astrophysics Technology (SAT) grant No. NNH177ZDA001N

PS-Contributed On Demand-184 Spatially Localized Etching using a Novel, Mask-free and Contactless Plasma Patterning Technique*, **Erik V. Johnson**, J. WANG, M. Ghosh, R. Leal, P. Bulkin, P. Roca i Cabarrocas,* LPICM-CNRS, Ecole Polytechnique, Institut Polytechnique de Paris , France*; S. Filonovich,* Total GRP, France

A novel, mask-free plasma-patterning technique has recently been demonstrated, allowing a lithographic function to be performed in a contactless manner [*R. Léal et al 2020 Plasma Sources Sci. Technol. 29 025023*]. This technique involves using a powered RF electrode containing grooves or slits (with widths in the mm or sub-mm range), as well as a custom-designed CCP-PECVD chamber. By approaching the RF electrode to within a very short distance of the substrate surface, plasma can be ignited and confined within the slits due to the hollow cathode effect. Therefore, the plasma process performed is spatially localized as well.

We present herein a further application of such mask-free, contactless PECVD process for the realization of spatially localized etching. A NF_3/Ar plasma chemistry has been employed, and different substrate materials (crystalline silicon, single layer and stacks of amorphous silicon thin films) have been tested. The patterned etching areas are first investigated by profilometry. In continuous mode, the etching rate is very fast (up to 10nm/s), making the controlled removal of thin films difficult, but by pulsing the RF power (duty cycles as low as 0.5%), the etching rate can be fine controlled down to around 1 Å/s, and a 3D mapping of the etching trench shows an excellent uniformity along its length. A further structural characterization has been performed within the etching trench by spectroscopic ellipsometry, before and after the etching process. The ellipsometric modelling results indicate that very little damage or surface roughening is induced by the pulsed etching process, despite the use of Ar in the gas mixture.

This work enables the application of this technique in the fabrication of semiconductor devices. For instance, the controllable etching rate and good etching homogeneity over large areas make it suitable for the formation of interdigitated contacts for the IBC solar cell, and we will present progress in this device application.

PS-Contributed On Demand-187 Effects of Outside Circuit on Capacitively Coupled Plasma Based on 1D Circuit Modeling and Experiments*, **Yuhua Xiao,*** North Carolina State University*; S. Nam, H. Lee, J. Lee,* Samsung, Korea (Republic of)*; S. Shannon,* North Carolina State University

Radio frequency capacitively coupled plasmas (CCPs) are widely used in etching and deposition processes. The applied voltage is mainly distributed over the sheaths formed near the powered electrode and the counter electrode. This counter electrode is typically grounded or isolated from ground through a dielectric break. The energy of ions hitting the electrodes is mostly determined by the properties of these sheaths. Manipulation of the constant and time dependent oscillation of these sheaths is the primary means to control the energy distribution of ions incident on the electrode surface. A widely used approach is using dual- or multi-frequency waveform generated by several power supplies. In this work, a simpler method is adopted to change the sheath voltages. A circuit consisting of a variable capacitor and an inductor connects to the floating electrode outside the reactor. The outside circuit changes the impedance between floating electrode and the ground, and the sheath voltage distribution therewith is modified. The plasma is simplified to an equivalent circuit model and adapted to simulate the effect of this outside circuit on sheath properties. The simulations are further compared to experimental results measured using hairpin probe, Langmuir probe, Voltage/Current probe, and a retarding field energy analyzer (Impedans Vertex RFEA). Results show that the outside circuit can partially control the DC self-bias and distribute the voltage and the energy loss between two sheaths associated with two electrodes. The outside circuit can enlarge the sheath volume adjacent to the floating electrode and reduce the sheath voltage of powered electrode prominently. These results point to possible source design based pathways for engineering the distribution of power dissipation across these sheaths in industrial plasma reactors.

PS-Contributed On Demand-190 Characterization and Spatially Resolved Analysis of an Open Channel Microfluidic Substrate for Atmospheric Plasmas*, **Josh Morsell**, S. Shannon,* North Carolina State University*; J. Jiang, P. Bruggeman,* University of Minnesota

The field of atmospheric pressure plasmas is an area of high interest. Many industries involving additive manufacturing, chemical processing and surface modification processes all stand to benefit from atmospheric plasmas. There are still many unknowns for how these plasmas interact with complex, multi-phase interfaces. The goal is to develop a controllable surface that is free from confounding issues with larger plasma-liquid interface experiments (i.e. convective stirring in bulk liquids). This work is for the design and characterization of an open channel microfluidics substrate for open use. The result is a series of 120 microchannels driven by capillary flow where flow characteristics are dependent on channel geometry. A rectangular cross section balances good performance with ease of manufacturing. The channels are 100um wide and 200um deep with a pitch of 100um. There are reservoirs on either end of the channels, one for fluid input and another for spatially resolved fluid extraction from the channels. It is possible to achieve a spatial resolution of 400um by utilizing per channel diagnostics. The device is etched via DRIE in a silicon wafer with a thermally grown oxide layer for chemical resistance. Flow measurements with these substrates show that a flow rate up to 1.2ml/min is possible and can be controlled by modifying applied pressure to the fluid inlet. A 13.56MHz atmospheric pressure plasma jet has been co-developed for studying the plasma-surface interactions. The designs for this microfluidic substrate are made available to the public for use. This work is supported by the DOE Center for Plasma Interactions with Complex Interfaces.

PS-Contributed On Demand-193 Construction of a Surrogate Model of a Plasma Processing Systemby Machine Learning*, **Masakazu Ichikawa, K. Ikuse,* Osaka University, Japan*; K. Chen,* National Yang Ming Chiao Tung University, Taiwan*; J. Wu,* National Yang Ming Chiao Tung University , Taiwan*; S. Hamaguchi,* Osaka University, Japan

The growth of semiconductor technology today is rapid and one of the challenges is to improve the productivity of semiconductor device manufacturing. Plasma processing is widely used in semiconductor device manufacturing and achieving more efficient real-time control of individual plasma processing tools on the manufacturing floor would vastly improve their productivity. Knowing the real-time physical parameters of a plasma processing tool would help improve the real-time control. Such parameters may include, for example, the electron density profile, ion energy and flux distributions, and etching rate profile over the wafer. In reality, however, because diagnostics that can access the plasma during the manufacturing process is extremely limited, one needs to rely on available tool data, such as input power, gas pressure, and possible additional sensor data, to make an educated guess on the current state of the plasma inside the tool. This is called virtual metrology (VM). To develop a VM system of a plasma tool, we are constructing a surrogate model of a plasma processing system based on numerical simulation data of the plasma. Such a surrogate model can be evaluated concurrently with the actual process, unlike the original physics-based numerical simulations. In this study, we used scikit-learn, an open-source machine learning library in Python, to predict various plasma parameters as functions of the powered electrode voltage and gas pressure for Ar plasmas. Data were obtained from two fluid-model-based plasma simulations and currently we are mostly focusing on one-dimensional simulations. Various techniques such as Lasso regression, Ridge regression, Gaussian process regression, and Multilayer perceptron have been tested for this problem. The results suggest that the plasma parameters can be predicted in real time and the model developed here is a stepping stone for an extension to 2 and 3-dimensional plasma simulation data in the future.

PS-Contributed On Demand-196 Incorporating Electronegative Feedback Mechanisms in a Global Plasma Circuit Model for Pulsed Power Delivery*, **Carl Smith,* North Carolina State University*; S. Nam, K. Bae, J. Lee,* Samsung Mechatronics R&D Center, Korea (Republic of)*; S. Shannon,* North Carolina State University

Pulsed inductively coupled plasma (ICP) sources have been of interest in the semiconductor industry over the past decade given their ability to reduce substrate damage and charge buildup. For an electropositive plasma, in the power ON-Cycle of a pulse, these discharges are typically characterized by a sharp increase in T_e, and n_e, as well as a corresponding decrease in the reflection coefficient (Γ) .. In previous work, a Matlab based Global Plasma Circuit Model (GPCM) has successfully been employed at characterizing these transients for Argon. This work presents experimental results from an SF_6/Ar Plasma taken on the Inductively Coupled Argon Oxygen System (ICAROS), where n_e was taken a photodiode as well as a time resolved hair pin resonator probe. Modifications to the equivalent transformer model are also proposed, such that electronegative effects such as electron attachment instabilities can be accounted for. Finally, the role that match effects has on inducing these electron attachment instabilities are also explored, as it has been observed that matching in the early ON-Cycle can induce these phenomena which are subsequently modulated by ratio of SF_6 to Ar. This work is supported by the North Carolina State University and the Samsung Mechatronics R&D Center

PS-Contributed On Demand-199 Comparative Study of Low Damage Plasma Etching Processes on the Integrity of AlGaN Layers Integrated in GaN HEMT During Gate Opening*, **Oleh FESIIENKO, C. Petit-Etienne,* University Grenoble Alpes, LTM, CNRS, France*; M. Darnon, A. Soltani, H. Maher,* Université de Sherbrooke, LN2, CNRS UMI-3463, Canada*; E. Pargon,* University Grenoble Alpes, LTM, CNRS, France

One promising integration scheme for High electron mobility transistors (HEMTs) based on III-N semiconductor heterostructures such as AlGaN / GaN is to use a thin AlGaN barrier. One of the fabrication challenges of this integration architecture is the etching of the SiN thin cap layer that must be stopped on the very thin 4 nm-thick AlGaN layer with a nanometer scale definition and without introducing damage and/or modification of the AlGaN surface layer.

In this work, the authors propose to investigate and compare different plasma etching strategies to etch the last 5 nm of the SiN cap layersanisotropically and with minimal damage to the thin layer of AlGaN material. Fluorocarbon and HBr-based plasma processes were developed in an inductively coupled plasma (ICP) reactor and compared to a digital etching concept that combines a SiN surface modification step by hydrogen ion implantation and a selective removal step of the modified SiN layer over the AlGaN using a Buffered oxide etching (BOE). The SiN modification depth during implantation is controlled by the hydrogen ion energy and flux. Post-etching treatments for repairing or minimizing the AlGaN surface damage induced by the SiN etching process were also evaluated. For all the cited strategies, the AlGaN surface damage in terms of chemical stoichiometry and change of the surface valence band energy were characterized by quasi in situ Angle Resolved X-ray Photoelectron Spectroscopy (AR-XPS), while the AlGaN surface roughness after process was analyzed by atomic force microscopy (AFM).

Concerning the preliminary results, we demonstrate that fluorocarbon plasma process has infinite SiN/AlGaN etch selectivity, due to the formation of an Al-Fx layer on the AlGaN surface that stops the etch. Unfortunately, the transformation of AlGaN surface into AlFx extends from 1.5 to 3.5 nm depth depending on the plasma ion energy, which is not acceptable when dealing with 4 nm thick AlGaN layer. Moreover, AlFx layer is hardly removed by wet or dry solutions. Upon HBr based plasma, the AlGaN surface stoichiometry is slightly degraded with Al and Ga depletion to a depth of 2 nm but without change of the valence band energy. Finally, the digital etching process was found to be the least damaging solution in terms of stoichiometry and valence band energy change. Complementary electrical characterizations will be performed to validate the use of the developed digital etching in the fabrication of high performant AlGaN/GaN HEMT.

PS-Contributed On Demand-202 Two-Dimensional Particle-in-Cell Simulation of Local and Nonlocal Electron Kinetics in Capacitively Coupled Plasmas*, **Hwan Ho Kim, C. Kim, J. Shin, H. Lee,* Pusan National University, Korea (Republic of)

In capacitively coupled plasma (CCP) systems operated under various pressure conditions in semiconductor and display manufacturing processes, physical phenomena are observed involving significant alterations in discharge characteristics, depending on local or nonlocal electron kinetics. The energy relaxation occurs locally or nonlocally depending on the electron energy distribution functions, and thus fluid models cannot treat these phenomena. Also, a one-dimensional particle-in-cell (PIC) simulation cannot capture the effects of the device structure, which is also an essential factor for plasma uniformity. Although a two-dimensional PIC simulation is required to this investigate these phenomena, it is challenging owing to high computational complexity and cost. For this purpose, we performed a parallelized two-dimensional PIC simulation with a graphics processing unit. We analyze the transition mechanisms of nonlocal and local electron kinetics and investigate the correlation with plasma uniformity for the variations of the driving voltage, gas pressure, the gap distance between upper and lower electrodes, and the boundary conditions.

PS-Contributed On Demand-205 Characterization of Plasma-Thermal Cu ALE Processes and Etch Products*, **Xia (Gary) Sang, J. Martirez, L. Bouchard, E. Carter, J. Chang,* University of California at Los Angeles

Chemical Mechanical Polishing (CMP) of copper (Cu) is reaching process limits as increasingly smaller feature sizes leave diminishing room for error for issues like dishing, defects, and corrosion. Plasma-thermal atomic layer etching of Cu is a promising and complementary process to address the challenges in nanometer-scale Back-End-of-Line (BEOL) device integration. This process consists of two steps: a modified layer is defined directionally in the plasma exposure step leveraging the anisotropic nature of low energy ions; the modified layer is completely and selectively removed by an isotropic etchant, leaving a final feature with ideal directionality.

This work achieves directional removal of Cu via the cyclic alternation of surface oxidation states. Low energy and directional oxygen ions were introduced to the surface, forming a thin film of oxidized copper. The oxide layer was then selectively removed, at a much higher rate compared to the metallic layer, using vapor phase formic acid. The surface composition changes after each process step were characterized by X-ray Photoelectron Spectroscopy (XPS) to delineate the formation of Cu2O, CuO and Cu(OH)2, corroborated by Cu LMM Auger lines. The etch product was collected and analyzed using Inductively Coupled Plasma Mass Spectroscopy (ICP-MS), Nuclear Magnetic Resonance (NMR) and Electron Paramagnetic Resonance (EPR) to confirm the presence of copper formate, the proposed reaction product. Experimental results were interpreted with the aid of density functional theory (DFT) calculations, which suggest the water-free dimeric tetra(μ-formato)dicopper(II) "paddlewheel" complex (Cu2(HCOO)4) to be the most favorable etching product. High resolution transmission electron microscope (HRTEM) images of a nano-scale patterned Cu thin film using this process confirmed the desirable, directional etch profile.

Plasma Science and Technology Division

Room On Demand - Session PS-Invited On Demand

Plasma Science and Technology Invited On Demand Session

PS-Invited On Demand-1 Control of Interface Layers for Selective Atomic Layer Etching*, Takayoshi Tsutsumi,* Nagoya University, Japan*; R. Vervuurt,* ASM, Japan*; N. Kobayashi, M. Hori,* Nagoya University, Japan **INVITED**

Atomic layer etching (ALE) processes with material selectivity are expected to be key to fabricate nano-sheet transistors, nanowire transistors and other three-dimensional devices. We have developed a plasma-enhanced ALE process using an energetic ion to form a self-limiting interface layer denoted by a modification or a mixture layer, which is sequentially removed by the plasma. This presentation focuses on the reaction mechanisms to achieve selective ALE processesfor silicon-compoundsby controlling the interface layer.

First discussed is the mixture layer formed by fluorocarbon plasma during the ALE of silicon oxide. We developed an atomic scale etching using alternating nanometer-thick fluorocarbon film deposition and O_2 plasma irradiation for silicon oxide.[1] The Ar ion enhances the reaction at the interface between the silicon oxide and fluorocarbon and forms a mixture layer which consists of carbon, fluorine, silicon and oxygen.. Therefore, control of the fluorocarbon film thickness and composition are required to improve repeatability of etched thickness per cycle and material selectivity in the process. The process achieved high process repeatability against cycle numbers because the O_2 plasma maintained a stable surface of the SiO_2, and removed excess carbon atoms as gaseous products such as CO. The O_2 plasma also initializes the chamber conditions in each cycle. We investigated the depth profiles of atomic concentrations in the mixture layer to improve the material selectivity.

Second discussed is the modification layer formed and by H_2 plasma and its removal step by fluorinated plasma.[2] We investigated the surface modification and etching mechanism by *in-situ* spectroscopic ellipsometry and attenuated total reflectance Fourier transform infrared (FTIR) spectroscopy.[3] The in-situ analysis clarified that the hydrogen plasma induced an increase in the concentration of Si−H and N−H bonds, and the N−H bond concentration plateaued more quickly than Si-H bonds. Considering the temporal change in the concentration of Si−H and N−H bonds during removal step by fluorine radical, Si−H bonds were primarily present near the surface, while N−H bonds were mainly located deeper into the silicon nitride film.

Based on the results, we will show understanding of the reaction mechanism helps to improve the controllability and the selectivity in ALE.

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PS-Invited On Demand-7 Current Modeling and Simulation Challenges of Low-Temperature Plasmas*, Anne Bourdon,* LPP, CNRS, Ecole Polytechnique, France **INVITED**

Low-temperature plasmas are used for applications ranging from material processing to bio-medical and electric propulsion applications. To model these discharges many physical and chemical processes have to be considered as multi-species nonequilibrium gas chemistry and transport, coupling of charged species with electromagnetic fields, coupling of the discharge with the fluid dynamics of the reactive gas, and coupling with surfaces and interfaces. For the modeling and simulation of these discharges, a major challenge is related to the very different space and time scales these processes may have. In the last decade, advances have been obtained on the mathematical modeling and high performance computing of low-temperature plasmas. In particular, the possibility to use multi-scale coupling methods, structured, unstructured, and adaptive mesh techniques, new algebraic equation solvers and parallel computing have opened a large range of new simulation possibilities. To illustrate some recent developments and current challenges in the field of modeling and simulation of low-temperature plasma discharges, two examples will be presented: fluid simulations of atmospheric pressure plasma jets for biomedical applications and plasma assisted combustion and PIC and fluid simulations of low-pressure magnetized plasmas for electric propulsion.

PS-Invited On Demand-13 Plasma-Substrate Interaction in the Case of Atmospheric Pressure Plasmas*, Ana Sobota,* Eindhoven University of Technology, Netherlands*; O. van Rooij,* Eindhoven University of Technology, Afghanistan*; M. Hofmans, O. Guaitella, A. Bourdon,* Ecole Polytechnique, Afghanistan*; P. Viegas,* Dutch Institute for Fundamental Energy Research (DIFFER), Afghanistan **INVITED**

Non-thermal plasmas are a versatile tool for applications at atmospheric pressure and in interaction with various substrates, but it has also been established that the substrates modify the plasma during the interaction. This work examines the effect on electron and heavy particle properties and discharge development.

PS-Invited On Demand-19 Recent Advances in Plasma Processing for the Creation of Tunable Biofunctional Surfaces and Interfaces*, Marcela Bilek,* *B. Akhavan, C. Tran, R. Walia, E. Kosobrodova,* University of Sydney, Australia*; A. Kondyurin,* university of Sydney, Australia*; C. Lotz, G. Yeo,* University of Sydney, Australia **INVITED**

Bio-functionalized surfaces are of great interest for a wide range of applications, particularly in biomedical diagnostics and implantable medical devices. We have shown that radicals embedded in carbon-rich surfaces facilitate simple, one-step surface-functionalisation [1]. The radicals are created by energetic ion bombardment of the surfaces. Reagent-free, covalent immobilisation of functional molecules occurs on physical contact by immersion or spotting / painting of the biomolecule-containing solutions onto the activated surfaces. This strategy simplifies covalent functionalisation of surfaces enormously and the approach can immobilise bioactive peptides, antibodies, enzymes, single stranded DNA, and extra-cellular matrix proteins [2] onto many materials, including polymers, metals and ceramics. Applications enabling biological studies of the response of individual cells to proteins on a sub-cellular scale [3], and the preparation of multi-functionalisable nanoparticles for theranostics [4] have been demonstrated. Spontaneous covalent immobilisation coupled with tuning of electric fields in double layers at the surface during the immobilization, created by pH variations and/or the application of external electric fields, enable control of the density and orientation of surface-immobilised bioactive peptides [5].

This presentation will review the underpinning science and report recent advances that extend the application of these techniques to functionalisation of the internal surfaces of complex, porous materials and structures using controlled flow fields and strategically designed electrodes to create plasma discharges within the internal spaces. The efficacy of embedded radicals to polymerise and covalently link hydrogels to solid surfaces and the use of atmospheric pressure plasma discharges to activate surfaces for covalent biofunctionalization during 3D bioprinting will also be explored.

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PS-Invited On Demand-31 Linear Hollow Cathode Plasma Source and the Deposition of Silicon Oxide Materials*, John Chambers,* AGC*; E. Michel, G. Arnoult,* AGC, Belgium **INVITED**

AGC's proprietary Linear Hollow Cathode electrodes are used to generate uniform linear plasma for PECVD.The patented technology drives pairs of electrodes using typical mid-frequency or pulsed-DC power supplies that are designed for magnetron sputtering.The linear hollow cathode technology uses electrode geometry to confine electrons and generate a dense plasma, and therefore does not require any magnetic field to maintain a linear discharge.

This novel plasma generation method allows for stable plasma discharge under a variety of process conditions -- notably under a wide range of process pressures.Since magnetic field is not necessary for plasma generation, other magnetic fields may be used to shape the plasma within the process chamber.

Additionally, the PECVD process allows for variation of plasma gas and precursor materials, as well as extreme variation in their flow rates and ratios.The combination of these process flexibilities allows for the deposition of materials with varied properties, such as silicon oxide materials of variable density and refractive index.

AGC Plasma Technology Solutions develops this technology for AGC’s own internal production processes, as well as for marketing outside of their glass coating industry for use in plate-to-plate and roll-to-roll coaters.

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PS-Invited On Demand-37 Co₂ Conversion in Microwave Plasma: Can We Bring It to an Industrial Scale?*, Floran Peeters,* Dutch Institute for Fundamental Energy Research, Netherlands **INVITED**

With increasing global interest in renewable energy technology, storage of electrical energy has become particularly relevant. The chemical industry must likewise be transformed to rely only on sustainably generated electricity to convert common molecules such as N_2 and CO_2 into chemical building blocks or fuels. Plasma-driven conversion has great potential for upscaling, since no rare materials are required in construction or upkeep, while also being compatible with the intermittent nature of sustainable electricity sources. Using plasma powered by microwaves, high power densities, and thus high throughputs, can be obtained. Moreover, since the plasma is essentially electrode-less, degradation of the reactor over time is virtually non-existent.

This contribution provides an overview of lab-scale results obtained from microwave plasma reactors. With a focus on CO_2 as the main input gas, a full description of the conversion process in these reactors will be given, pieced together from gas composition and temperature diagnostics, combined with both gas flow and chemical kinetic modeling. The importance of transport of both species and heat to and from the plasma will be highlighted.

Using the insights gained from these experiments and models, strategies for further improvement of the conversion process will be sketched. Included in this analysis are the potential for heat recycling and heat integration to improve energy efficiency in the plasma, the energy costs involved in peripheral processing steps such as expansion or compression of the feedstock gas, and the possibilities for integrating the separation of product species such as O_2 and CO from the output gas stream. A rough cost calculation will be used to assess to what extent plasma might be used to turn CO_2 into a chemical building block.

PS-Invited On Demand-43 2021 AVS PSTD Young Investigator Award Talk: Plasma Treatment on SiGe for Improvement of Interface Trap Density by Inducing Si Segregation*, Yohei Ishii*[1], Hitachi High-Tech America, Inc.*; R. Sugano,* Hitachi, Ltd., Japan*; Y. Lee, W. Wu,* Taiwan Semiconductor Research Institute, Taiwan*; H. Ishimura,* Hitachi High-Tech Taiwan Corp., Taiwan*; K. Maeda, M. Miura,* Hitachi High-Tech Corp., Japan **INVITED**

Transistor structure was modified from planar into Fin-type Field Effect transistor (FinFET), in order to improve short-channel effects due to the device scaling. Although FinFET has been widely applied recently, further scaling is still required to follow Moore’s law. However, the continuous scaling is getting more challenging due to the reality approaching toward atomistic-level control of pattern pitch. One of the methods to enhance electrical performance in FinFETs is the use of silicon (Si) in n-FETs and silicon germanium (SiGe) in p-FETs due to the higher hole mobility [1]. This is one of the promising candidates for sub-10nm process.

In order to enhance SiGe characteristics in addition to the use of SiGe, reducing interface trap density is critical for sub-threshold improvement [2]. This can be achieved to produce Si-rich surface at SiGe/gate-oxide interface on SiGe surface, because unstable GeO_x leads to charge trap defects at the interface [3]. There are two processes used conventionally to realize the Si-rich surface: atomic layer deposition of Si cap over SiGe fin [4] and GeOx scavenging process [3]. However, these methods require the use of high temperature, which may bring about strain relaxation in the SiGe channel and Ge diffusion into Si substrate. To avoid the deterioration of the SiGe characteristics, low temperature process is desirable. However, the SiGe composition control at low temperature process has not been studied yet.

In this study, we developed low-temperature plasma treatment that induces Si-rich modification layer on SiGe surface. We revealed that the mechanism to realize the Si-rich surface is caused by Si segregation behavior under the plasma treatment experimentally. We will also present that the surface composition modulation was energetically favorable using ab-initio calculation. The details of the plasma treatment is further discussed experimentally, in conjunction with ab-initio calculation.

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PS-Invited On Demand-55 Going Mobile: Design, Optimization, and Scaleup of Plasma Reactors for Treatment of Pfas-Containing Ion Exchange Brine*, Selma Mededovic Thagard,* Clarkson University **INVITED**

Poly- and perfluoroalkyl substances (PFAS) have recently received considerable attention due to their toxicity, ubiquitous presence and recalcitrance in the environment. Current large-scale treatment of groundwater contaminated with PFAS involves using an ion exchange (IX) resin. In regenerable IX systems, the regeneration of the resin yields still bottoms or brine, a complex and highly electrically conductive chemical mixture of high concentration PFAS, methanol (usually recovered by distillation), and sodium chloride that is expensive to dispose of and often must be stored on-site. A promising solution to the disposal of brine is through plasma-based water treatment, a low-cost, low energy process which has been demonstrated to be extremely efficient in degrading a range of PFAS.

In this work, we have adapted a proven plasma-based treatment system for low concentration, low conductivity PFAS-contaminated water so that it can treat regenerant brine. A bench-scale point-point discharge reactor was developed to investigate the influence of solution electrical conductivity and ion composition on the performance of the reactor in treating a single PFAS-perfluorooctanoic acid (PFOA)-in a solution containing sodium chloride that was used to adjust the solution conductivity between 0.3 and 45 mS/cm.The influence of various ions was explored using chlorine and non-chlorine salts to adjust the conductivity.

Following bench-scale investigations, the reactor was upscaled for the treatment of large volumes of brine. A “high-concentration” and a “low-concentration” bench-scale batch plasma reactors were developed and used successfully to degrade PFAS at high concentration (>100 mg/L) and low concentration (< 1 μg/L), respectively, in still bottom solutions

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[1] **PSTD Young Investigator Award**

containing numerous PFAS with a wide concentration range. The reactors were installed into a mobile trailer and demonstrated in the field earlier this year at an Air Force Base.

PS-Invited On Demand-61 Plasma Process Requirements for Emerging Memories*, **Nicole Saulnier**, I. Saraf, A. Dutta, K. Brew, S. Mehta, P. Jamison, O. van der Straten, I. Ok, S. Seo, C. Silvestre, C. Yang, M. Rizzolo, S. Choi, H. Chen,* IBM Research Division, Albany, NY*; P. Adusumilli,* IBM Research Division, T.J. Watson Research Center*; J. Arnold,* IBM Research Division, Albany, NY*; D. Edelstein,* IBM Research Division, T.J. Watson Research Center*; J. Slaughter,* IBM Research Division, Albany, NY*; T. Ando,* IBM Research Division, T.J. Watson Research Center*; A. Sebastian,* IBM Research GmbH, Zurich Research Laboratory **INVITED**

The industry is experiencing a surge of interest in new memories, and their integration with logic devices. Some of this interest is driven by the slowdown in traditional device scaling, which is creating opportunity for fast, dense, low power memory that can be closely coupled to processors without consuming precious silicon area. Another very powerful driver of interest in non-traditional memories is Analog Artificial Intelligence (AI), where there is tremendous potential for speed and energy efficiency improvements by using arrays of non-volatile multi-state memory elements to store the weights linking nodes within neural networks.

Both applications for emerging memories have a distinct set of device metrics which must be met to achieve the desired technology performance. These device metrics can be sensitive to the applied processes and introduce new requirements for the plasma processes used to deposit materials, pattern structures, treat surfaces, etc. For the analog AI application space, devices should have low stochasticity and low variability across a range of states. A population of devices should be able to be programmed into each desired state and should remain in that state until it is intentionally updated. Both phase change material (PCM) devices and Resistive RAM (RRAM) devices are susceptible to plasma processes during device integration. For a more traditional memory application, device metrics are relaxed since the device needs to achieve only two states. These states are typically far enough apart that concern of overlap is low. However, these devices need to be densely packed so they tend to have smaller CD and pitch compared to devices being considered for analog AI applications. One example of an emerging memory that is considered as an SRAM or DRAM replacement is Magnetoresistive RAM (MRAM). The small geometry and complex materials stack used for MRAM devices can be a challenge for integration and patterning. In addition to these applications introducing new requirements, many of these memory devices involve the introduction of materials not typically used in semiconductor devices. Emerging memories which introduce new sensitivities and/or new materials will drive a need for new processes, chemistries, and tools to achieve efficient, high yield, and scalable fabrication.

This paper will present a handful of case studies, each of which examines an emerging memory device. The new device's requirements will be reviewed, along with the current common practices for fabrication. Discussion of the limitations of those current processes will highlight opportunities for further research and development.

This work was performed by the Research Alliance Teams at various IBM Research and Development Facilities

Materials and Processes for Quantum Information Science Focus Topic
Room On Demand - Session QS-Contributed On Demand

Materials and Processes for Quantum Information Science Contributed On Demand Session

QS-Contributed On Demand-1 Power and Temperature Dependence of High Q Superconducting Resonators*, **Ashish Alexander**, C. Weddle, C. J. Richardson,* Laboratory for Physical Sciences, University of Maryland, College Park, MD

An integrated temperature and power dependent model of a resonator internal quality factor predicts the loss contribution from two-level systems and quasiparticles simultaneously in a superconducting resonator. At millikelvin temperatures, the sub-gap microwave photons due to resonator readout signal drive the quasiparticle number and phonon density far from the thermal equilibrium corresponding to the bath temperature. Here we propose a two-temperature, power and temperature dependent model to evaluate resonator losses that define the driven quasiparticle density by a distinct effective temperature than the bath temperature. The contribution of the readout power for different power and temperature is also explored. Resonators fabricated from epitaxial molecular beam epitaxy grown aluminum on float-zone refined silicon are evaluated to have quality factors above 1M. These results are analyzed with the proposed model and the contribution of various loss mechanisms is explored.

QS-Contributed On Demand-4 A Density-Functional Theory Study of the Al/AlO$_x$/Al Tunnel Junction*, **Chang-Eun Kim**, K. Ray, V. Lordi,* Lawrence Livermore National Laboratory

The aluminum oxide tunnel junction is a key component of superconducting quantum devices. The quantum coherence time of the aluminum oxide tunnel junction has seen five orders of magnitude improvement over the last twenty years, however, it is still too short to realize a scalable quantum computer. We asked what may be still limiting its further improvement. We used ab-initio calculations to develop a realistic model of the tunnel junction and compared to experimental observations known to date. The ab-initio electronic structure result shows that under-coordinated Al ion forms conducting channel, effectively rendering the true thickness of the insulating part of tunnel junction significantly thinner than what may be measurable under electron microscopes. The computed properties of amorphous junction are compared to a series of ideal crystalline junction models with variable thickness, highlighting what would be possible if we had better control over the interface microstructure of the tunnel junctions. Electron tunneling of model junction is probed by solving Schrödinger equations (SE) using the potential obtained from ab-initio result, revealing channel formation and inhomogeneous tunneling transport that is correlated to the thickness distribution. The detailed theoretical description of the widely used aluminum oxide tunnel junction, along with the ab-initio-based systematic approach to predict the performance of tunnel junction, will further strengthen our understanding of this critical materials system that is indispensable to realize superconductor-based quantum computing devices. (Prepared by LLNL under Contract DE-AC52-07NA27344)

QS-Contributed On Demand-7 A Cold Atom Interferometry Sensor Platform Based on Diffractive Optics and Integrated Photonics*, J. Lee, R. Ding, H. McGuinness, J. Christensen, R. Rosenthal,* Sandia National Laboratories, USA*; G. Biedermann,* University of Oklahoma*; S. Kemme, D. Gillund, A. Ison, G. Hoth, B. Little, D. De Smet, C. Walker, A. Kodigala, M. Gehl, E. Skogen, M. Eichenfield, A. Lentine, **Peter Schwindt**,* Sandia National Laboratories, USA

Keywords—atom interferometer; cold atoms; magneto-optical trap; integrated photonics

We report the current progress in the development of a compact, deployable cold atom interferometry sensor platform, which could be generally applied to cold-atom gravimeters, accelerometers, gyroscopes, and clocks. Our effort targets the miniaturization of key components of the sensor platform and includes significant engineering efforts in the development of grating-mirror magneto-optical traps (G-MOTs), vibration-resistant structural design, custom titanium vacuum package with passive pumping, silicon-photonic multi-channel on-chip single sideband modulators, and a feedforward technique to extend the dynamic range of the atom interferometer inertial sensors.

We will highlight the development of a compact cold atom sensor head for measuring acceleration. Laser light is brought to the sensor head via optical fiber to perform the functions of laser cooling and trapping, the atom interferometer three pulse laser sequence, and atomic state sensitive detection. The atoms are contained in a custom Ti vacuum chamber (volume of ~90 cm^3), and we demonstrated a G-MOT where the grating is inside the chamber. Finally, we discuss the results of the atom interferometric acceleration measurements with sensor head.

We have also developed the Ti vacuum chamber that it is only passively pumped; no active pumping is required to maintain the vacuum for a cold-atom trapping. Excluding the grating and using sapphire windows, we have demonstrated a MOT in the passively pumped chamber for nearly one year with no apparent degradation in the vacuum quality.

For extreme system miniaturization, there are significant efforts in the development of heterogeneously integrated photonic integrated circuits (PICs) for the cold atom sensor using silicon photonics, amplification with III-V gain materials, and second harmonic generation. We demonstrated a four-channel optical single sideband (SSB) modulator on a silicon PIC at 1560 nm with a high extinction ratio and a high carrier-injection modulation, which can dynamically control laser frequencies and intensities during the experimental sequence of a cold atom interferometer. We envision a fully integrated system, in which 30 on-chip SSB modulators can be applied to a 6-degree-of-freedom (DOF) matterwave inertial measurement unit (IMU). Such a PIC-based system could shrink the size of the typical laser system for an atom interferometer from the size of an optical table to tens of cm^3.

This work 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. This paper describes technical results and analysis. Any subjective views or opinions that might be expressed in the paper do not necessarily represent the view of the U.S. Department of Energy or the United States Government.

QS-Contributed On Demand-10 Observation of the Two-Photon Transition and Bloch-Siegert Shift of the Electrically Detected Magnetic Resonance Spectrum of Interface Defects in 4H-SiC Metal-Oxide-Semiconductor Field-Effect Transistors*, James P. Ashton, P. Lenahan,* The Pennsylvania State University

We report on the observation of multiple-photon transitions in the electrically detected magnetic resonance (EDMR) spectrum of interface defects at the 4H-SiC/SiO$_2$ interface. Multiple-photon transitions are important for quantum engineering as they have been linked to spin-based quantum computation for coherent manipulation of spin-qubits [1]. These observations are made possible with the utilization of a new EDMR scheme that incorporates an RF frequency sweep with the sample held at constant ultra-low magnetic field B_0 instead of a magnetic field sweep at constant RF frequency. The latter is the traditionally utilized EDMR scheme known as continuous wave (cw) EDMR. In the frequency-swept (fs) EDMR spectrum, the two-photon transition emerges because of ultra-strong coupling effects between the spin system and the driving field B_1 which provides the RF radiation. fsEDMR measurements are made in the sub-mT regime, where the Zeeman interaction is weak. Sub-mT EDMR measurements using a cwEDMR approach would be difficult as there is an oftentimes pervasive near-zero field magnetoresistance (NZFMR) effect that occurs in the sub-mT range [2]. Thus, the fsEDMR scheme is useful in such measurements since the NZFMR response can be eliminated by sweeping the RF frequency instead of sweeping the B_0 field. We utilize the fsEDMR scheme to validate that the transitions we observe are caused by multiple-photon transitions. In a fsEDMR spectrum, these transitions occur at integer divisions of the resonant frequency where in a magnetic field sweep scheme, the transitions occur at multiples of the resonant magnetic field. In this way, we rule out the possibility of harmonic detection of the resonant frequency caused by the apparatus. The two-photon line shape is analyzed as a function of the B_1/B_0 and it is found that spectral narrowing occurs as the ratio B_1/B_0 is increased. This observation is consistent with recent theoretical work provided by Mkhitaryan *et al.* [3]. The fsEDMR response is also slightly shifted off resonance due to the Bloch-Siegert shift [4]. We confirm the observation of the Bloch-Siegert shift via an extraction of B_1 and compare it to the value B_1 extracted using a sniffer test coil. Within experimental error, the values of B_1 extracted using both techniques are the same.

This work at Penn State was supported by the U.S. Army Research Laboratory.

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QS-Contributed On Demand-13 Tunable Filters and Parametric Amplifiers from NbTiN Transmission Line Resonators*, R.M. Lewis, W. Kindel, L. Tracy, C. Harris, T. Lu, D. Luhman,* Sandia National Laboratories, USA

Quantum computing applications require that control signals be carefully filtered to minimize noise reaching the qubits. Quantum limited amplification of output signals is also used to reduce readout time. We present measurements of non-linear NbTiN resonators which are useful as both tunable bandpass filters and as parametric amplifiers.

Transmission line resonators make excellent bandpass filters. Here we demonstrate that such filters made from NbTiN are tunable by pumping a higher or lower harmonic of the resonator. We present data for a resonator with a full line width of ~ 150 kHz which is tunable by several MHz. We demonstrate a tuning of many linewidths and achieve an on/off ratio of ~ 30 dB. Further exploiting the nonlinearity of the NbTiN, this resonator exhibits gain of nearly 15 dB when pumped near the critical power at which bifurcation occurs.

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-NA-0003525.

QS-Contributed On Demand-16 Nv Center Generation by Electron Beam Excited Plasma*, Akihito Saeki, A. Chikamoto,* Meijo University Graduate School, Japan*; P. Abraha,* Meijo University, Japan

The nitrogen-vacancy (NV) centers, point defects in diamond, have a property of photoluminescence useful for sensors in the field of quantum life science. The NV centers must be highly sensitive for use in the measurements of exothermic energy of proteins such as enzymes in cells. The sensitivity of NV centers can be increased through the near-surface formation of NV centers and increased number density. This research details the simultaneous formation of the vacancy and annealing processes performed by electron irradiation.

Currently, NV centers have been created by annealing after electron irradiation of 200 keV to 10 MeV onto the synthetic diamond surface. However, the energy of the irradiated electron is excessively large, which severely damages the surface.

In this research, experiments were conducted by irradiating the diamond surface with accelerated electrons using an electron beam excited plasma system. The system allows for controllable delivery of energy and density of the accelerated electrons. Here, NV centers are formed by electron irradiation while simultaneously annealing the diamond surface through electron collision that heats the surface. Photoluminescence using a Raman spectrometer confirms the formation of NV centers. The treated diamond showed peaks of NV center emission at around 637 nm. The peak intensities increased gradually with the applied energy and density of the irradiated beam. In this presentation, the gradual increase in the fluorescence intensity at 637 nm for the varying electron energy and electron density of the electron beam excited plasma will be shown.

QS-Contributed On Demand-19 Strain-Induced Interdiffusion in III-V Compound Semiconductors for Quantum Structure Formation*, **Leonid Miroshnik**,* Chemical & Biological Engineering, University of New Mexico*; B. Rummel,* Nanoscience & Microsystems Engineering, University of New Mexico*; A. Li,* Chemical & Biomolecular Engineering, University of Pennsylvania*; G. Balakrishnan,* Center for High Technology Materials, University of New Mexico*; T. Sinno,* Chemical & Biomolecular Engineering, University of Pennsylvania*; S. Han,* Nanoscience & Microsystems Engineering, University of New Mexico

We demonstrated stress-directed compositional patterning in compound semiconductors as a novel method to form quantum structures[1-4]. This is a significant departure from the traditional methods of forming quantum structures, such as strain-driven Stranski-Krastanov growth or solvothermal synthesis. In this work by applying a thermo-mechanical stress field, we are expanding the idea to III-V compound semiconductors, where InGaAs on GaAs is our model system. The approach allows for 3D quantum structures to be scalably manufactured. We characterized the atomic interdiffusion in the InGaAs/GaAs model system. Understanding the behavior of non-Fickian diffusion as a function of strain provides a pathway to design systems where patterned stress fields under thermally activated conditions can be used to produce 3D spatially ordered quantum structures. Previous studies provided a large uncertainty in calculated Arrhenius diffusion coefficients, and there is a disagreement on the effects of strain in diffusion.Measuring the interdiffusion parameter is extremely sensitive to the processing and characterization conditions. Molecular beam epitaxy (MBE) was used to grow high-quality quantum wells with well-defined concentration profiles. The structures were annealed in a rapid thermal annealer (RTA) and analyzed using Secondary Ion Mass Spectroscopy (SIMS). This characterization technique provides precise information on the composition on the angstrom scale. In this presentation, we show our processing, annealing and characterization technique provides a high accuracy repeatable compositional profile. In addition, we have developed a multiscale computational model that couples continuum methods with coarse-grained lattice kinetic Monte-Carlo to extract stress mediated diffusion parameters and to predict the time evolution of technologically relevant compositions.

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Materials and Processes for Quantum Information Science Focus Topic
Room On Demand - Session QS-Invited on Demand

Materials and Processes for Quantum Information Science Invited On Demand Session

QS-Invited on Demand-1 Quantum Matter, Simulation, and Clock*, Jun Ye,* JILA and University of Colorado Boulder **INVITED**

Precise engineering of quantum states of matter and major advances in optical coherence and laser technology are elevating the performance of optical atomic clocks to new levels. A low-entropy Fermi gas of Sr atoms loaded into a three-dimensional optical lattice represents a powerful platform to discover, understand, and utilize many-body quantum systems that are metrologically powerful and lay the foundation for the connection between quantum simulation and quantum sensing. These increasingly powerful measurement capabilities are promising greater opportunities for probing fundamental and emerging phenomena.

QS-Invited on Demand-7 Photonic Interfaces for Ion-trap Quantum Computers*, Tracy Northup,* University of Innsbruck, Austria **INVITED**

Trapped ions are among the most promising quantum computing platforms, but there are technical limits to the number of ions, and thus the number of quantum bits (qubits), that can be stored in a single trap. One approach to scale up the number of qubits beyond these limits is to link together multiple ion-based processors in a network via photonic quantum interfaces. I will describe how optical cavities provide efficient quantum interfaces between ions and photons and how we integrate these cavities with ion traps. An important materials question is whether the presence of dielectric cavity mirrors compromises the computing performance of nearby ions. To address this question, I will present recent work in which we model and experimentally measure the heating rate of a trapped ion placed in the vicinity of a cavity mirror. This work not only has implications for ion-based quantum networks but also may provide new insight into the heating mechanisms in microfabricated ion traps.

QS-Invited on Demand-13 Empowering Quantum Photonics with Nanoplasmonics and Machine Learning*, Vladimir Shalaev,* *A. Boltasseva,* Purdue University **INVITED**

New approaches to address major challenges in quantum photonics by employing plasmonic metamaterials and machine learning will be discussed.

QS-Invited on Demand-19 Engineering Silicon Qubits at the Atomic Scale*, Sven Rogge,* University of New South Wales, Australia **INVITED**

Spins in silicon are attractive candidates for scalable quantum information devices, because of their long coherence times and potential for high-density integration. This talk focuses on challenges in scaling from the device to the circuit level. While quantum information devices in spin based systems have been shown to be promising, the small dipole moment of spins make interaction of multiple qubits challenging to implement. Recently, artificial spin-orbit coupling induced by micro-magnets in double quantum dot devices has been successfully implemented to couple spin qubits in silicon to a microwave cavity on the single photon level. The presence of intrinsic spin-orbit coupling in acceptors however, could allow for fast quantum-gate manipulations and effective long-range inter-qubit coupling with a simple device layout. Recent acceptor qubit proposals suggest the possibility of maintaining the dipole moment between the spin-orbit states, without suffering from short coherence times. By coupling a bulk 28Si crystal to a superconducting coplanar waveguide resonator, we measured a coherence time (T2) of 0.7 ms for an acceptor spin ensemble in bulk 28Si crystal under strain. This value for this coherence time is over 4 orders of magnitude higher than previously found in boron-doped silicon devices, and demonstrates the potential of boron-based acceptor spins in silicon as a candidate for scalable, electrically-driven qubits with long coherence times. The second part of the talk focuses on single dopant atom placement. Atomic-scale engineering reached a level of control where single-atom devices can be reproducibly fabricated. The indirect band gap of silicon and the resulting valley degree of freedom has been considered to be challenging for donor qubit architectures. This is due to the fast oscillations of the valley component of the donor wave function that is incommensurate with the silicon lattice. Single-electron spectroscopy maps obtained on fully integrated donor devices in ultra-high vacuum allow a direct measurement of the valley phase difference between two donors. Such quantum-state images of two-donor devices led to a donor based two qubit gate design that is robust in regard to variability in dopant placement.

QS-Invited on Demand-25 Reproducible Superconducting Circuits for Quantum Information Processors*, Eric Zhang,* IBM T. J. Watson Research Center **INVITED**

Superconducting quantum processors based on fixed-frequency transmon architectures are attractive for their simplicity of fabrication and long coherence times. However, the frequency precision of as-fabricated transmon qubits range from 1 - 2%, which results in significant frequency crowding and reduced two-qubit gate-fidelity. In this talk, we describe selective laser annealing to assign transmon frequencies into desired frequency patterns and describe both the practical (~18 MHz) and fundamental (~5 MHz) precision of the laser annealing process. We combine precision studies with Monte-Carlo yield modeling to ascertain the desired tuning performance metrics required for high-yield of collision-free chips. We will present laser-annealing on our largest multi-qubit processor to date, our 65-qubit Hummingbird processor, with a post-annealed median two-qubit gate fidelity of 98.7%. As a scalable post-fabrication frequency trimming technique, we anticipate laser-annealing to play a central role in the production and scaling of high-fidelity superconducting quantum processors up to and beyond 1000-qubit levels.

Acknowledgements The authors acknowledge support under IARPA (Contract No. W911NF-16-1-0114) for collision yield modeling and multi-qubit device characterization.

QS-Invited on Demand-31 Materials Loss Measurements Using Superconducting Microwave Resonators*, Corey Rae McRae,* NIST Boulder / CU Boulder **INVITED**

Two level system (TLS) loss in dielectric materials and interfaces remains at the forefront of materials research in quantum information science. The identification of low loss fabrication techniques, materials, and thin film dielectrics is critical to achieving scalable architectures for superconducting quantum computing. Superconducting microwave resonators provide a convenient qubit proxy for assessing loss performance and studying loss mechanisms such as TLS loss, non-equilibrium quasiparticles, and magnetic flux vortices. In this talk, an overview of design considerations for accurate resonator loss measurements will be given, summarizing techniques that have been evolving for over two decades, and will conclude with recommendations for future measurements in this field.

QS-Invited on Demand-37 Organic Color Center: A New Class of Quantum Materials*, Han Htoon,* Los Alamos National Laboratory **INVITED**

Color centers in diamond and SiC are now standing as a key material system for realization of quantum information technologies ranging from ultrasensitive sensing of electric/magnetic fields to eavesdropping-proof communication and quantum computing.Recent studies have shown that defects capable of mimicking some of the key quantum mechanical properties of these color centers can also be created via covalent bonding of organic functional groups onto the side-wall ofSWCNTs.Here in this talk I will provide a brief over view on our recent accomplishments in understanding and controlling quantum optical properties of these covalent defects, which are often referred to as “organic color centers.”[1] Firstly, I will describe our low temperature single defect PL and magneto PL spectroscopies revealing a molecularly tunable electronic structure of these defects[2] and magnetic brightening of spin-sensitive optical transitions. Secondly, Hanbury-Brown-Twiss quantum optic experiment demonstrating the first room temperature single photon generation in O- to C- telecom optical wavelength bands with 99% single photon purity will be presented.[3,4]I will then provide an update on integration of these quantum defects into photonic, plasmonic and electronic nano devices.[5,6] Finally, I will report our most recent Hong-Ou-Mandel quantum optic experiment performed on quantum defects coupled to plasmonic cavities.We were able to realize indistinguishable single photon generation by exploiting the Purcell enhancement of the radiative decay rate of individual defects.[7]

[1] Nat. Photon 11, 535 2017; [2] ACS NanoNat. Chem. 10, 1089 2018; [3] Nat. Photon. 11, 577 2017; [4] Nat. Mater. 17, 663 2018;

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SE-Contributed On Demand-1 Electrodeposition of Mn^{+3} Rich Layered δ-Phase Mno$_2$ Nanofibers on Epitaxial Graphene-Silicon Carbide Heterostructures for Fast Selective Gas Sensing*, Michael Pedowitz, S. Kim,* Department of Electrical and Computer Engineering, University of Maryland, College Park*; B. Uppalapati,* 3Holcomebe Department of Electrical and Computer Engineering, Clemson University, Clemson*; D. Khan,* Holcomebe Department of Electrical and Computer Engineering, Clemson University*; F. Bayram, G. Koley,* Holcomebe Department of Electrical and Computer Engineering, Clemson University, Clemson,*; R. Myers-Ward,* Naval Research Laboratory, USA*; K. Daniels,* Department of Electrical and Computer Engineering, University of Maryland, College Park

Mixed valence manganese oxides (MnO$_x$) have attracted significant research interest in recent years due to the easily reversible redox reactions between manganese oxidation states (Mn^{+2}, Mn^{+3}, and Mn^{+4})[1] which enable applications in catalysis[2], energy storage[3], and gas sensing[4]. Of the MnO$_x$ compounds, manganese dioxide (MnO$_2$) has been of particular interest due to its wide variety of structural polymorphs, which allow for enhanced control over the available surface area and reactive properties of MnO$_2$. Among these crystalline phases, the δ-phase contains a large number of Mn^{+3} defects, as Mn^{+3} content has been found to increase the catalytic activity of MnO$_2$ films we selected the δ-phase to be the optimal phase to produce highly reactive MnO$_2$ thin films[5]. However, MnO$_2$'s reactivity is limited by its low inherent conductivity[4]. To overcome this limitation, heterostructures have been formed between MnO$_2$ and graphene, seeking to couple the conductivity of graphene with the reactivity of MnO$_2$. We selected quasi-freestanding epitaxial graphene on silicon carbide (EG/SiC) as the substrate for the electrodeposition. In this work, we present the electrodeposition of δ-MnO$_2$ on (EG/SiC) and then demonstrate its reactive properties by processing the resulting film into a room temperature gas sensor. The electrodeposition was carried out in a three-electrode electrochemical cell with an Ag/AgCl reference electrode, a Pt counter electrode, and an EG/SiC working electrode utilizing 0.1M manganese acetate solution. The resulting δ-MnO$_2$/EG/SiC was then characterized through Raman spectroscopy, photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), and atomic force microscopy (AFM) to determine its crystalline phase and surface morphology. Raman spectroscopy confirmed the formation of δ-MnO$_2$, and the XPS indicated it was Mn^{+3} rich with an average oxidation state of 3.3. The SEM revealed that the surface was made up of microplates ~160µm^2 coated in nanofibers in nanofibers. AFM confirmed this and indicated the nanofibers were ~10nm thick. Following characterization, we deposited 4 Ti/Au(30nm/120nm) contacts on the δ-MnO$_2$ to form a simple gas sensor that was tested against 5ppm NO$_2$, 5ppm NH$_3$, 1000ppm IPA, and 1000ppm methanol. In preliminary room temperature testing, the sensor displayed a response time <2s for NO$_2$ and NH$_3$ and no response for IPA and methanol, demonstrating the reactive potential of the produced heterostructure.

References:[1]L. Spinelle et al.*Sensors* 17(7), 1520(2017)[2] F. Cheng et al. *Chem. Mater* 22(3), 898-905(2010)(3) Y.J. Huang et al. *Electrochim Acta* 99, 161-165(2013)[4]N. Joshi et al. *Microchim. Acta* 185, 213(2018)[5]Z. Chang et al. *Proc Natl Acad Sci USA* 115(23), 5261-5268(2018)

SE-Contributed On Demand-4 Fabrication of Hydrogenated Tungsten Carbide Coatings by Reactive Superimposed Hipims-Mf Deposition System: Effect of Target Poisoning Ratio*, B. Lou,* Chang Gung University, Taiwan*; I. Moirangthem, **Jyh-Wei Lee,*** Ming Chi University of Technology, Taiwan

The research of tungsten carbide coatings has attracted lots of interest from academia and industry due to their outstanding properties such as high hardness, high wear resistance, chemical stability and low coefficient of friction. In this study, the hydrogenated tungsten carbide coatings were fabricated by a superimposed high power impulse magnetron sputtering (HiPIMS)- middle frequency (MF) deposition system. The W target poisoning status was controlled using a plasma emission monitoring (PEM) system by adjusting the gas flow ratios of Ar and acetylene (C_2H_2). The morphology and microstructure of coatings were evaluated by scanning electron microscope (SEM) and transmission electron microscope (TEM). The crystallinity of films was studied using an X-ray diffractometer (XRD). The electron probe micro analyzer (EPMA)was used to determine the chemical compositions of thin films. The hardness, adhesion and tribological properties of coatings were explored. The corrosion resistance of tungsten carbide coated AISI304 stainless steel plates was evaluated in 0.1 M H_2SO_4 solution. We found that the peak power density of the HiPIMS increased with increasing target poisoning ratio. The deposition rates and carbon concentrations of coatings also increased with increasing target poisoning ratio. The crystalline β-WC$_{1-x}$ phase was transformed into an amorphous phase when target poisoning ratio of coating increased from 50% to 70%. We can conclude that the hydrogenated tungsten carbide coating with the highest hardness of 32.3 GPa, high critical load (L_{C1}) of 34.3 N, high resistance to plastic deformation index (H^3/E^{*2}) of 0.53, excellent corrosion resistance, and a quick deposition rate of 21.9 nm/min/kW was grown by the superimposed HiPIMS-MF power supply at the target poisoning ratio of 30% in this work.

SE-Contributed On Demand-7 In-Situ Raman Approaches for Studying Tribological Surfaces*, Andrey Voevodin, A. Shirani, E. Cairns, K. Jacques, M. Dockins, A. Killam, S. Aouadi, D. Berman,* University of North Texas*; J. Mogonye, S. Berkibile,* DEVCOM Army Research Laboratory

The study provides examples of in-situ Raman spectroscopy use to investigate adaptive tribological surfaces lubricated with solid and liquid materials. The in-situ Raman spectroscopy is shown to capture tribologically induced changes of adaptive surfaces inside the lubricated sliding contact in response to applied mechanical and thermal stresses. For solid lubricated adaptive contacts, duplex plasma-electrolytic oxidation (PEO) and chameleon coating produced on Al alloys were investigated. These were composed of a 80-160 mm thick hard load-supporting Al-Si-O coating and a 5–8 µm top layer of a chameleon coating made of graphite or BN, MoS_2 or WS_2, and Sb_2O_3. For liquid contacts, 52100 steel coupons were tested under lubricant starvation regimes using low viscosity hydrocarbons. The counterpart pins were made of 52100 steel and Si_3N_4. The tests were performed at temperatures ranging from room (liquid lubrication) to 600 °C (solid lubrication). In-situ Raman spectroscopy revealed that the lubricating phases, i.e. MoS_2, WS_2, and graphite, were protected from oxidation by the porous PEO structure. It also revealed a gradual evolution of chameleon composition with diminishing orthorhombic Sb_2O_3 phase presence at the surface in favor of hexagonal lubricating phases of chameleon components. The low shear strength of MoS_2, WS_2, and graphite and the integration of the chameleon coating with the PEO sublayer were responsible for the ultra-low friction behavior. In all examples, the in-situ Raman spectroscopy was shown to reliably detect contact chemical change correlated with the observed friction behavior.

SE-Contributed On Demand-10 Advances in Fatigue Testing of Protective Coatings: A Case Study on Cr-Based Ceramics*, L. Zauner, R. Hahn,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria*; M. Alfreider,* Department of Materials Science, Montanuniversität Leoben, Leoben, Austria*; P. Polcik,* Plansee Composite Materials GmbH, D-86983 Lechbruck am See, Germany*; O. Hunold,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; D. Kiener,* Department of Materials Science, Montanuniversität Leoben, Leoben, Austria*; **Helmut Riedl,*** Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria

Thermomechanical fatigue phenomena strongly limit the life time of modern high-performance components and therefore demand innovative coating materials extending the life-time through predictable crack propagation. Especially, an in-depth knowledge on the decisive failure criteria of ceramic thin film materials – generally associated with an intrinsic lack in ductility – under long-term mechanical loading is paramount to enhance limited bulk material properties. Literature reports on fatigue resistance, especially of hard coatings but also thin films in general, are relatively rare. Thus, an extensive analysis of different coatings – meaning prevalent bonding states, i.e. altered ratio of ionic, covalent, or metallic bonds – with respect to fatigue phenomena (e.g. LCF, HCF, or extrusion formation) is of great interest.

Within this study we present a methodical approach towards a general understanding on the failure behaviour of PVD deposited thin films from the aspect of the bonding nature between the atomic constituents using model systems – Cr and Cr-based ceramics, respectively. The DC magnetron sputtered thin films were analysed with respect to structure, thermo-mechanical properties, and morphology by means of micro-mechanical testing, X-ray diffraction, as well as electron imaging techniques. The influence of the stress state was quantified through high-temperature wafer-curvature measurements. Static fracture characteristics such as fracture toughness KIC and -stress σf have been evaluated during cantilever bending of pre-notched beams. Low and high cycle fatigue tests of unstrained micro-cantilevers were subsequently performed under various loading scenarios based on the critical stress intensities observed during the quasi static tests. These results are also correlated with dynamic-mechanical analysis to get insights on the size effects during fatigue testing. Through this comprehensive approach we are able to identify the most critical aspects with respect to fatigue life of these protective coating materials.

Keywords: Fatigue; Thin films; Cr-based compounds; Micro cantilever; LCF; HCF

SE-Contributed On Demand-13 Structural, Nanomechanical and Tribological Properties of Plasma Electrolytic Oxide Coatings for Sliding Contact Applications*, **Esteban Broitman,*** SKF B.V. , Netherlands*; J. Dzwonczyk-Mertzanis, S. Geerts,* SKF B.V., Netherlands*; G. Dennis,* SKF Ltd., UK

Plasma electrolytic oxidation (PEO) is a method that promotes the formation of a high-hardness ceramic coating on the surface of light metals. The process involves an anodic oxidation of the metallic substrate by subjecting the alloy to high voltages in an electrolytic bath.

In this work, PEO Keronite® coatings were fabricated on a AA7075-T73 aluminum alloy. This lightweight surface finishing solution is targeting self-lubricating sliding contact applications where conditions request low to medium ranges of loads and medium to high motion frequencies.

The microstructure and composition of the as-received coatings were characterized by SEM and EDS. Nanomechanical properties (hardness H_{IT} and elastic modulus E_{IT}) were studied by nanoindentation on samples cross-sections confirming a bi-modular coating composition. Toughness and macroscale hardness were derived from classic Vickers indentation. The sliding friction and wear responses were assessed by pin-on-disc tests where the counterface was a commercial lining compound available on the market for self-lubricating applications. Furthermore, the coated samples were also characterized by an oscillating dynamic load test that replicates load behavior from real applications. In addition, a modeling exercise has been performed to analyze distribution of contact pressures in the system with a coated interface. The tribological results obtained on Keronite® were compared to an electroless Ni plated coating, highlighting pros and cons of this type of coating being used for self-lubricating sliding applications.

SE-Contributed On Demand-16 The Struggles to Compare Coatings Hardness by Vickers and Instrumented Nanoindentation Techniques*, **Esteban Broitman,*** SKF B.V., Netherlands

It is widely accepted to define the hardness of a solid material as its resistance to a permanent shape change when a constant compressive force is applied. At macro- and microscale, the Vickers hardness test is assessed from the size of an impression left under a load by a four-sided pyramid-shaped diamond indenter. The Vickers hardness number, H_V, is then calculated as the indenter load L divided by the actual surface area of the impression A_c measured after the indentation. On the other hand, the instrumented nanoindentation hardness H_{IT}, using a three-sided pyramid-shaped diamond indenter, is calculated as the maximum indenter applied load L_{max} divided by the projected area of contact at maximum load A_{pml} , i.e., during the indentation [1].

There are many publications where authors try to compare their coating hardness values measured by nanoindentation with bulk hardness values that have been measured by Vickers tests. The comparison is usually made through a formula that is supposed to give an exact mathematical equivalence of hardness values between both methods: $H_V = 0.09\ H_{IT}$, with H_V having units of kgf/mm^2 and H_{IT} having units of MPa. In this presentation, I demonstrate that an exact mathematical equivalence can be established only for materials with 0% indentation elastic recovery. In other cases, I will show that it is impossible to establish such mathematical relationship.

[1]"Indentation Hardness Measurements at Macro-, Micro-, and Nanoscale: A Critical Overview" Esteban Broitman - Tribology Letters 65 (2017) 23.

SE-Contributed On Demand-19 Alloying of Period VI Transition Metal Boride-Based Coatings for Ultra-High Temperature Oxidation Protection*, **Thomas Glechner,** R. Hahn, A. Bahr,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria*; T. Wojcik,* Institute of Materials Science and Technology, TU Wien, Austria*; M. Weiss,* Institute of Chemical Technologies and Analytics, TU Wien, Austria*; J. Ramm, O. Hunold,* Oerlikon Surface Solutions AG, Liechtenstein*; S. Kolozsvári,* Plansee Composite Materials GmbH, Germany*; H. Riedl,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria

Various challenges in the field of environmental sustainability as well as emission reduction in general are closely linked to the usage of ultra-stable materials. Protective coatings sustaining harsh environments, involving highest temperatures accompanied by abrasive and corrosive media, are therefore of great interest. Transition metal ceramics are a suitable class to resist such conditions. Especially, period VI borides, nitrides and carbides stand out due to their extraordinary mechanical properties and highest thermal stabilitymaking them interesting for ultra-high temperature applications. However, their high temperature stability is strongly limited due to their strong tendency to form volatile oxides.

In particular, to improve the oxidation resistance of period VI based transition metal diborides, it is important to first have a profound knowledge on the scale formation of the binary systems – such as HfB_{2-z}, TaB_{2-z} and WB_{2-z}, in oxidative environments. Here, especially the influence of the stoichiometry and constitution of the grain boundary interior is of major interest. Based on that knowledge, we developed alloying strategies which tremendously enhance the oxidation resistance of these coating materials and enable temperature regimes up to 1600 °C. The coating materials were deposited using an unbalanced magnetron sputtering system and consequently oxidized in a DTA/TG setup (using coatings on substrates) to study the oxidation kinetics. These results were verified with long-term oxidation tests at 1200 °C (various time periods up to 60 h) using a conventional chamber furnace. To gain a comprehensive insight on the relation between chemical composition, crystal structure, as well as morphology, we applied a broad set of high-resolution characterization techniques (e.g. HR-TEM, APT, SIMS, as well as XRD) to correlate the as deposited with the annealed states.

SE-Contributed On Demand-22 Influence of the Nature of the Terminal Group on the Rate of Tribochemical Reaction of Carboxylic Acids on Copper*, **Resham Rana,** W. Tysoe,* University of Wisconsin Milwaukee

Lubricant additives reduce friction and wear by reactively forming a thin tribofilm at the rubbing contacts in machines. Carboxylic acids are often used as both boundary lubricants and also as lubricant additives that undergo tribochemical reactions to form a tribofilm on the surfaces. It has been suggested that the terminal group on the carboxylic acids could influence their tribochemical reaction rate. This was studied on a well-characterized clean copper sample in an ultrahigh vacuum tribometer capable of measuring friction, load, and electrical contact resistance to follow the tribochemical reaction by analyzing the surface by microfocus Auger electron spectroscopy. An atomic force microscope (AFM) is also used to measure the friction, and pull-off forces, and tribochemical reaction rates of a carboxylic acid on a copper (100) surface. The microscale tribochemical reactions are carried out using a tungsten carbide ball under a normal load of ~0.44 N, and the nanoscale tribochemical reactions with a silicon tip applying a normal load of ~56.0 nN where both result in similar contact stresses. C-C, C=C, and C≡C terminated carboxylic acids were studied and no effect on the tribochemical reaction rates was found despite the difference in friction and pull-off forces being measured in AFM.

SE-Contributed On Demand-25 Enhanced Oxidation Resistance of Cr_2AlC MAX Phase Coatings through Tailoring of Substrate Microstructure*, **Clio Azina,*** Materials Chemistry, RWTH Aachen, Germany*; J. Gonzalez-Julian,* Forschungszentrum Jülich GmbH, Germany*; P. Eklund,* Thin Film Physics Division, Linköping University, Sweden*; J. Schneider,* Materials Chemistry, RWTH Aachen, Germany

MAX phases are a family of layered ternary ceramics, characterized by a hexagonal structure, which are considered for high temperature applications. In particular, Al-based MAX phases have attracted significant attention because of their self-healing behavior. Indeed, weakly-bonded Al is able to diffuse and react with the oxidizing atmosphere to form a protective Al_2O_3 scale. In the case of Cr_2AlC, the loss of Al, which leads to the formation of the alumina scale, is accompanied by the local decomposition of the MAX phase into Cr_7C_3 just below the Al_2O_3 scale resulting in the formation of pores in the vicinity of the interface. The presence of pores has an adverse effect on the mechanical and thermal stability of the component and often results in its premature failure. To avoid the Cr_7C_3 formation, Al would need to be supplied to the oxide scale continuously. To this end, we deposited Cr_2AlC coatings on Cr_2AlC substrates and focused on the interfacial interaction to prove the concept of continuous Al supply from the Cr_2AlC substrate to the Cr_2AlC coating.

Cr_2AlC substrates were produced by spark plasma sintering of either elemental or Cr_2AlC powders. The substrates produced contained different amounts of secondary phases and exhibited different grain sizes. Cr_2AlC coatings were deposited on the produced substrates using high power pulsed magnetron sputtering (HPPMS) to obtain dense films. The Cr_2AlC / Cr_2AlC assemblies were then oxidized at 1100 °C in air for different times to investigate the effect of the microstructural variations of the substrate on the oxidation behavior.

SE-Contributed On Demand-28 Corrosion Induced Diffusion Pathways in Thin Film Materials Investigated by Atom Probe Tomography*, Oliver E. Hudak*, *E. Aschauer,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria*; V. Dalbauer,* Department of Materials Science, Friedrich-Alexander-Universität Erlangen-Nürnberg, Germany*; L. Shang, O. Hunold, M. Arndt,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; P. Polcik,* Plansee Composite Materials GmbH, Germany*; P. Felfer,* Department of Materials Science, Friedrich-Alexander-Universität Erlangen-Nürnberg, Germany*; H. Riedl,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria

Corrosion phenomena have a large impact in almost all of today's technological fields. A ubiquitous interplay between material and its environment challenges material-engineers in selecting materials that provide a safe and work effective implementation. In this regard, protective thin films and surface modifications have opened up new avenues in aviation and power generation sectors. In particular, physical vapor deposited (PVD) coatings have been specifically developed to elicit superior material properties, as well as extend the longevity and work performance of machining components. Unfortunately, due to a deficient understanding of corrosion related processes in PVD coatings, industrial demands for high performance corrosion resistant thin films remain sparse.

This study intends to take a closer look at corrosion driven diffusion pathways in aqueous solutions at an atomic scale. As many technical alloys used in marine environments, aviation and energy sectors are prone to pitting corrosion, a demand for tailored corrosion protective coatings seems quite overdue. A three-electrode cell potentiostat was utilized for conducing potentiodynamic polarization measurements, and enabled precise control over the corrosion test parameters. With a systematic approach on highlighting preferred diffusion pathways, this study displays a thorough exploration of the effect of grain size, macro-particle formation and crystallinity on the diffusion mechanism in arc-PVD thin films. For better tracing the corrosive species, a novel marker architecture was developed for eliciting chemical and structural changes upon arrival of the diffused media. Consequently, this allows for improved application of high-resolution analytical methods, such as APT and TEM, to help identify preferential diffusion paths.

Keywords: Corrosion resistance; PVD coatings; Diffusion pathways; Atom probe tomography; pitting corrosion

SE-Contributed On Demand-31 Effects of Magnetic Field Strength on the Structure and Properties of non-hydrogenated DLC Coatings Deposited by HiPIMS*, Jianliang Lin,* Southwest Research Institute, San Antonio Texas*; X. Zhang,* Southeast University, China

In this study, non-hydrogenated diamond like carbon (DLC) coatings (3-4 mm) were deposited by sputtering a graphite target in argon (Ar) using high power impulse magnetron sputtering (HiPIMS). The effects of the vertical magnetic field strength (B) in the middle of the target racetrack on HiPIMS deposition parameters, and structure and properties of the DLC coatings were investigated. The coatings were characterized by transmission electron microscopy (TEM), Raman spectroscopy, atomic force microscopy (AFM), scratch test, nanoindentation, and ball on disk wear test. It was found that the deposition at a higher B was associated with a higher peak target current density and an increased ion flux to the substrates. These conditions are beneficial for improving the structure and properties of DLC coatings. The DLC coatings deposited at a higher B exhibited more compact surface, smaller carbon mounds and a higher sp^3 bond fraction. The results showed that a B higher than 600 G is needed for obtaining dense DLC coatings with a high sp^3 bond fraction and a high hardness (>35 GPa). However, the deposition rate of DLC coatings decreased as B was increased. The tribological properties of the coatings were evaluated under dry and lubricated conditions. The tribological tests revealed great friction reduction and improved wear resistance of these non-hydrogenated DLC coatings deposited by HiPIMS.

SE-Contributed On Demand-34 Enhancing the Surface Properties of Polymethyl Methacrylate by TiO_2 Atomic Layer Deposition*, Mina Shahmohammadi*, *E. Pensa, H. Bhatia, B. Yang, G. Jursich, C. Takoudis,* University of Illinois - Chicago

Polymethyl methacrylate (PMMA) is a widely used polymer in applications such as engineering structural plastics, energy storage materials, and biomaterials. However, its poor surface properties and wear resistance lead to fracture and deformation. Functionalization of the PMMA surface can make it stable in aggressive environments and prevent it from biodegradation, discoloration, and increased surface roughness. Here, thermal Atomic Layer Deposition (ALD) was used to deposit TiO_2 thin films from Tetrakis(dimethylamido)titanium(IV) (TDMAT^{TM}) and ozone (O_3) on PMMA substrate, without the need for plasma assistance or alumina interlayer, to improve its surface properties. The depositions were done in a commercial ALD system (Kurt J. Lesker ALD150LE$^{TM)}$. The reactor pressure and temperature were kept at 120°C and 1 Torr, respectively and ultra-high purity N_2 was used for both carrier and purging gas. Spectroscopic ellipsometry was used to measure the film thickness on thick PMMA substrate and two different growth regimes were observed for initial and later ALD cycles. Initially, the growth rate on PMMA was 1.39 Å/cycle, which is ~3.5 times higher than that on silicon (0.4 Å/cycle). However, after ~30 nm-thick film on PMMA, the growth rate became similar to that on silicon. Moreover, our results revealed that the presence of PMMA affects the growth rate on silicon reference. These findings were corroborated with Residual Gas Analyzer and X-ray Absorption Near-Edge Structure data. The thermal stability of the PMMA samples used in this study, was examined by Thermogravimetric Analysis. Chemical composition and surface roughness of coated PMMA were studied by X-ray Photoelectron Spectroscopy and optical profilometry, respectively, which corroborated the presence of a uniform conformal film of TiO_2. The TiO_2 coating increased wettability by ~70% and surface hardness by 60%.

SE-Contributed On Demand-37 Development and Scale-up of ALD Coatings for Sulfur Tolerant, Long Lifetime Catalyst Powders*, Christopher Gump*, *J. Burger, D. Lindblad, G. Rojas, K. Buechler,* Forge Nano*; W. McNeary,* National Renewable Energy Laboratory (NREL)

As potential applications of atomic layer deposition expand beyond the nano-scale devices of the semiconductor industry, development of larger-scale processes on high surface area substrates are necessary.This is especially true in catalyst coating applications, where ALD has been shown to improve stability, selectivity, and lifetime of catalyst materials. The high surface areas associated with supported catalysts introduce new challenges with regards to processing.

As a part of an effort to improve sulfur tolerance and lifetime in supported palladium catalysts for biomass processing, we used ALD to deposit under- and over-coatings of alumina or titania onto Pd/Al_2O_3- and Pd/TiO_2-supported catalysts. Because of the high surface area of the substrates (140 - 185 m^2/g), even low numbers of ALD cycles required large amounts of deposition precursors and resulted in high weight loadings of film on the catalyst. Initial small-scale tests performed on 3 g lots of catalyst powder resulted in 5-15wt% mass gains with fewer than 10 ALD cycles. Precursor transport was a rate limiting step for the deposition, and controlled dosing of the precursor was critical to achieving reproducible deposition.

Using the hydrogenation of naphthalene to tetralin as a model reaction, the productivity, conversion, and turn-over frequency of the coated catalysts was characterized.The titania overcoat on the Pd/Al_2O_3 proved to be the most effective catalyst, increasing the productivity, conversion, and turnover frequency in the model reaction. Although the film increased catalyst performance, carbon monoxide chemisorption testing indicated that the ALD film reduced the number of available Pd metal sites on the catalyst.

The TiO_2 overcoat on Pd/Al_2O_3 was scaled up from the 3 g lot size to a 100 g lot size (~15,000 m^2 of powder surface area). Coating this quantity of powder required the implementation of a large-scale precursor vaporizer capable of delivering the tens of grams of the titanium (IV) isopropoxide used as the titanium source every cycle. The TiO_2-coated catalyst coated at the large scale showed the same increase in productivity, as well as increased stability after 450 or 750°C thermal treatments, as compared to the uncoated materials. The TiO_2-coated catalyst also retained the highest amount of activity (86%) after sulfur poisoning by dimethyl disulfide.

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Advanced Surface Engineering Invited On Demand Session

SE-Invited On Demand-1 Metallic Glass: A Novel and Emerging Coating For Various Industrial Applications*, P. Yiu,* ***Jinn P. Chu,*** National Taiwan University of Science and Technology, Taiwan **INVITED**

In this presentation, I will first present many unique properties that make thin-film metallic glasses (TFMGs) stand out from other thin film materials: smooth surface, ultra-low coefficient of friction, low surface free energy, non-sticking surface, high plasticity, anti-cell adhesion properties, biocompatibility, and shape recovery. I will also demonstrate a number of applications where TFMGs have outstanding performance over the existing materials, such as surgical blades and various types of diffusion barriers that boosted the lifetime of their corresponding device. We also showcase a number of innovative attempts to put TFMG in commercial products and industrial applications.Furthermore, we would like to showcase that due to the variety of composition and thus properties of TFMGs, they have a wide range of applications from consumer products like kitchen cutlery to the cutting edge MEMS, to be explored. The ease of TFMG fabrication by magnetron sputtering is also favorable for industries and manufacturers to transfer the technologies from laboratory to factory. Our research and development of TFMG is still ongoing and making a remarkable progress and hopefully it could open up even more new research works in the near future. In addition, new perspectives in the research and development of TFMGs and opportunities for commercialization will also be highlighted.

Smart Multifunctional Materials for Nanomedicine Focus Topic
Room On Demand - Session SM-On Demand
Smart Multifunctional Materials for Nanomedicine Contributed On Demand Session

SM-On Demand-1 Cisplatin-Loaded Palladium Nanoparticles for Cancer Nanomedicine*, L. Cucci, A. Bellissima,* University of Catania, Italy*; T. Marzo, D. La Mendola,* University of Pisa, Italy*; V. Notarstefano, E. Giorgini,* Polytechnic University of Marche, Italy*;* ***Cristina Satriano,*** University of Catania, Italy

In this work, a PdNP@CisPt hybrid based on palladium nanoparticles and cisplatin was developed. Nanoparticles were synthetized via a modified redox chemistry green method, based on D-glucose and PVP as reducing and capping agents, respectively. The CisPtwas immobilized by a physisorption protocol. The characterization of the new hybrid was carried out by UV-visible spectroscopy, to correlate the changes in the plasmonic peak to the interaction of the drug with the PdNP surface, and by AFM and DLS measurements, to get insight into the morphology and size of the functionalized nanoparticles. Additionally, an ICP-AES investigation was carried out to assess the precise Pd to Pt ratio. Results confirmed the strong association of the drug to the nanoparticle surface.Noteworthy, the CisPt activity is often associated with the appearance of several side effects due to its non-specific action, including neurotoxicity, nephrotoxicity and ototoxicity [1]. On the other hand, nanomaterials have a demonstrated capability to overcome the inherent limitations of conventional drug, improving the solubility of hydrophobic molecules, increasing their half-life and selectively, thereby enhancing the therapeutic effects and diminishing the side effects [2-3]. Our cellular experiments on prostate cancer cells (PC-3 line) demonstrated that the developed systems significantly reduced cell migration (scratch test), with a synergistic action of PdNP and CisPt in the PdNP@CisPtagainst PC-3 cells. Moreover, the PdNP@CisPt showed an effective antitumour action (cell viability tests). In cell micro-Raman analyses confirmed the PdNP and PdNP@CisPt cellular internalization at the nuclear level, with a deep alteration in nucleic acids and proteins conformation and relative amount. To scrutinize the antitumor mode of action of PdNP, known to involve the interactions of the nanoparticles with the functional groups of proteins and the phosphate groups of DNA, the leakage of lactate dehydrogenase and the generation of reactive oxygen species (ROS), the xanthine oxidase assay was performed. Results confirmed an increase of ROS species generation. Cell imaging by confocal microscopy showed perturbation in mitochondrial staining, related to oxidative damage, as well as in the intracellular copper accumulation.

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SM-On Demand-4 A Multifunctional Plasmonic Nanoplatform of Hyaluronan-Decorated Nanoparticles Fabricated by Atmospheric Plasma for Angiogenic and Antibacterial Applications*, V. Caruso,* University of Catania, Italy*; D. Merche, J. Baneton, A. Ozkan,* Université libre de Bruxelles, Belgium*; L. Cucci,* University of Catania, Italy*; R. Inturri, G. Galizia,* Fidia Farmaceutici S.p.A, Italy*; S. Godet, L. Malet, F. Reniers,* Université libre de Bruxelles, Belgium*; S. Vaccaro,* Fidia Farmaceutici S.p.A., Italy*;* ***Cristina Satriano,*** University of Catania, Italy

Plasmas at atmospheric pressure is a simple, fast and versatile method for the synthesis of noble metal nanoparticles (NPs), such as nanosilver (Ag NP) and nanogold (Au NP) [1]. Biomolecules and natural polymers are often used as stabilizer and capping agent during the nanoparticle synthesis, to enhance their biocompatibility as well as targeting capability. In this study, hybrid systems made of an Au or Ag NP metal core capped by a soft shell of hyaluronan (HA) polymer were fabricated by the microplasma method, with reduction of the metal precursor salts in HA aqueous solution. Hyaluronan has excellent properties of water solubility, biocompatibility, biodegradation, non-toxicity, and non-immunogenicity [2]. The multifunctional character of the HA@NP nanoplatforms resulted from the combination of the optical features of the plasmonic nanoparticles as well as their intrinsic biological properties (i.e., angiogenic regulation for Au NP and antibacterial activity for Ag NP, respectively [3]) with the properties of HA, used in the MW range from 200 to 1200 kDa (low-MW HA is angiogenic and high-MW HA is anti-angiogenic [4]). The HA@NP systems were characterized, in the comparison with both bare NPs and the analogous hybrids synthetized via a chemical route, by UV-visible spectroscopy and dynamic light scattering to study the plasmonic properties of hyaluronic acid hybrids with metallic nanoparticles as well as their stability during the aging time. The cytotoxicity of the nanoplatforms was evaluated by MTT assay on the HUVEC cell line. Furthermore, their influence on the wound healing process was examined by microbiological studies on pathogenic bacteria strains of *E. coli* and *S. aureus*.

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SM-On Demand-7 Angiogenin-Functionalized Gold Nanoparticles-Graphene Oxide Nanohybrids for Wound Care Application*, L. Cucci, L. Riela,* University of Catania, Italy*; O. Hansson,* University of Gothenburg, Sweden*; T. Marzo,* University of Pisa, Italy*; C. Satriano,* University of Catania, Italy*;* ***Diego La Mendola,*** University of Pisa, Italy

In this work, we tackled the controlled assembling of gold nanoparticles (AuNP) and graphene oxide (GO) nanosheets at different C/O ratio, followed by their surface tailoring with the angiogenin (ANG) protein.

The Au-GO-ANG nanocomposite, by exploiting the synergic effects of antioxidant and antiangiogenic AuNP [1], antimicrobial GO [2] and angiogenic ANG [3], is a very promising platform to achieve a modulation of the angiogenic process in the wound healing treatment. The Au-GO-ANG hybrids were characterized by UV-visible spectroscopy, to scrutinise the ANG binding to Au-GO, by monitoring the changes in the nanogold plasmonic peak, as well as in the graphene pàp* transition electronic band, respectively. Atomic force microscopy and dynamic light scattering analyses confirmed a strong association of the protein to both the plasmonic nanoparticles and the nanosheets.The interaction of Au-GO-ANG at the biointerface with supported lipid bilayers, inspected by means of the acoustic sensing technique of quartz crystal microbalance with dissipation monitoring, pointed to a strong perturbation of model cell membranes compared to what found with the reference nanosystems without the protein. Cellular experiments on fibroblasts and endothelial cells demonstrated the low cytotoxicity of the hybrid assemblies and their high ability to promote wound closure and cell migration. The activity of Au-GO-ANG were also tested in the presence of copper ions, that can modulate protein signaling pathways. 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 multifunctional biomaterials Au-GO-ANG for wound care treatment and tissue regeneration.

The authors thank M-era.Net project SmartHyCAR ('Smart Multifunctional Hyaluronic Acid-Carnosine Based Bandages for Wound Care and Regenerative Therapy'; Reference Number: project 4274) and University of Catania (Piano della Ricerca di Ateneo, Linea di Intervento 2, 2018–2020) for their financial support.

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SM-On Demand-10 Hyaluronan-Metal Gold Nanoparticle Hybrids for Targeted Tumour Cell Therapy and Antibacterial Applications*, Vanessa Sanfilippo*, *L. Cucci, V. Caruso,* University of Catania, Italy*; R. Inturri, L. Messina, S. Vaccaro,* Fidia Farmaceutici S.p.A., Italy*; T. Fontaine, A. Demaude, F. Reniers,* Université libre de Bruxelles, Belgium*; C. Satriano,* University of Catania, Italy

In this work, a multifunctional nanoplatform based on core-shell nanoparticles of antiangiogenic gold nanoparticles (AuNP) [1] capped with low molecular weight (200 kDa) hyaluronic acid (HA) was assembled at room temperature via a green, one-pot redox synthesis method [2]. HA, the main component of the extracellular matrix, is utilised to bioengineer nanoparticles for active targeting, owing to its high affinity in binding the CD44 cell receptor. A dielectric barrier discharge (DBD) plasma at atmospheric pressure [3]was used to obtain plasma-activated hyaluronic acid (p_HA), either in the presence or in the absence of Cu^{2+} (copper is also a known bactericidal agent). Different plasma parameters, including the plasma power and the carrier gas were varied.The HA- and p_HA-conjugated gold nanoparticles were scrutinised by UV-visible spectroscopy, dynamic light scattering and atomic force microscopy, which all pointed to the effective 'surface decoration' of the gold nanoparticles by hyaluronan chains. The CD44-targeting capability of HA-functionalized gold nanoparticles was tested in terms of both cytotoxicity and antibacterial activity. Cell viability assays were performed on two CD44-positive cell models, namely prostate tumour (PC-3) cells and normal human umbilical vein endothelial (HUVEC) in comparison with neuroblastoma cells (SH-SY5Y), which do not express the CD44 receptor. Results demonstrated, upon the cellular treatments by the hyaluronan-functionalized nanoparticles, an increased cytotoxicity in neuroblastoma than in prostate cancer cells compared to the bare, glucose-capped AuNP. A receptor-dependent perturbation effect on both cytoskeleton actin and lysosomal organelles was detected by scanning confocal microscopy. Cell migration studies (scratch test) on PC-3 and HUVEC confirmed the promising potentialities of the plasma technique to modulate the hybrid biointerface between the bioengineered nanoparticles and the cells. On the other hand, an enhanced inhibitory activity was found for HA-capped AuNP against both Gram-negative *Escherichia coli*and Gram-positive *Staphylococcus aureus*. These findings demonstrated the very promising potential of HA–AuNP systems for selective cytotoxicity in cancer therapy with an anti-angiogenic effect tuned by a controlled perturbation of cell migration processes in cancer metastases.

M-era.Net project SmartHyCAR ('Smart Multifunctional Hyaluronic Acid-Carnosine Based Bandages for Wound Care and Regenerative Therapy'; Ref N.: 4274) and University of Catania (PIAno di inCEntivi per la RIcerca di Ateneo 2020/2022 CHANCE_Linea di Intervento 1 e GRABIO_Linea di intervento 2) are acknowledged for their financial support.

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Surface Science Division
Room On Demand - Session SS-Contributed On Demand
Surface Science Contributed On Demand Session

SS-Contributed On Demand-1 Development of Low Thermal Budget Si Epitaxy and High-K/Metal Gate Stack for Atomically Precise Electronic Devices*, Evan M. Anderson,* *D. Campbell, J. Ivie, S. Schmucker, P. Lu, X. Gao, L. Tracy, R. Arghavani, E. Bussmann, A. Baczewski, T. Lu, D. Ward, S. Misra,* Sandia National Laboratories

Atomic precision advanced manufacturing (APAM) uses a scanning tunneling microscope to create donor devices in an atomically thin layer doped beyond the solid solubility limit, enabling unique device physics. This presents an opportunity to investigate digital electronics at the atomic limit. APAM has been excellent for producing one-off devices for physics experiments, but many materials challenges must be resolved before integration with industry standard metal-oxide-semiconductor (MOS) technology. A functional device, such as a transistor, additionally requires epitaxial Si to cap and activate the dopants and a gate on the surface to control it. Low thermal budget (LT) processes are needed to limit dopant diffusion to preserve atomic precision, though this introduces defects in the materials and interfaces.

The parameter space for optimizing LT epitaxy is large and material characterization is difficult, making the path forward unclear. Transmission electron microscopy (TEM) indicates the LT epitaxy yields minimal structural defects, while secondary ion mass spectrometry (SIMS) reveals impurities. However, the subtle variations within these observations do not reliably correlate with Hall measurements of the donor layer, making the importance of these defects ambiguous. To resolve this, we have separately developed an LT high-k/metal gate stack to produce MOS capacitors to study the defects in the APAM donor layer, epitaxial Si, and Si/oxide interface. The gate stack is of sufficient quality that C-V characteristics are dominated by the underlying LT epitaxial layers. C-V measurements of MOS capacitors consisting of LT epitaxial Si and the APAM donor layer provide densities of electrically active defects introduced by LT epitaxy that can be correlated to TEM and SIMS. This combination of tools allows thorough understanding of the impact of LT epitaxy parameters on device performance, enabling optimization the LT epitaxial Si for integration of industry compatible MOS technology with APAM devices for atomically precise digital electronics.

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SS-Contributed On Demand-4 Mechanisms of Electrocatalytic Reduction of N_2 at Vanadium and Cobalt Oxynitride Surfaces: Impacts of Metal Oxophilicity and Π-Backbonding*, Adaeze Osonkie*, *A. Ganesan, P. Chukwunenye, F. Anwar, I. Rashed, F. D'Souza, T. Cundari, J. Kelber,* University of North Texas

The electrochemical nitrogen reduction reaction (NRR) is an environmentally and energy-friendly alternative to the Haber-Bosch process for the production of NH_3, which currently accounts for 2% of the world's energy usage. While earth-abundant catalysts, especially transition metal oxides and oxynitrides, have received intense recent scrutiny, there is little fundamental understanding of basic reaction mechanisms at the electrolyte/surface interface; including the roles of N-metal vs. O-metal interactions, or of metal-N_2 interactions. We present here a comparison between oxophilic vanadium oxides/oxynitrides and cobalt oxynitride. Vanadium is more oxophilic, while Co ions exhibit higher d-orbital occupancy. Herein, electrochemical, absorption spectroscopy, and XPS measurements, supported by DFT calculations for vanadium oxide and oxynitride films, are compared to those for cobalt oxynitride films. All films were formed by magnetron sputter deposition. Electrochemical and absorption spectroscopy data demonstrate (a) N_2 reduction in vanadium oxides and oxynitrides occurs primarily at O-supported V centers; and (b) NRR activity for cobalt oxynitrides indicates ~ one order of magnitude increase in activity relative to the vanadium systems, as well as evidence of high selectivity for NRR vs. the hydrogen evolution reaction (HER) under identical conditions. DFT calculations indicate that both N_2 absorption and reduction at O-supported vanadium sites (V_O) is energetically favored over N-supported (V_N) centers, but that this difference in energies should decrease sharply for less oxophilic systems, such as Co. Initial calculations also suggest that the order-of-magnitude enhanced NRR activity and selectivity for the cobalt oxynitride film is due to increased 3d-orbital occupancy vs. the vanadium systems, resulting in enhanced π-backbonding and more facile protonation of adsorbed N_2.Implications of these results for future studies and the design of Earth-abundant NRR-selective catalysts will be discussed.

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SS-Contributed On Demand-7 Advanced Thermoporometry Characterization of Disordered Mesoporous Materials*, **Henry R. N. B. Enninful**, D. Schneider, R. Kohns, D. Enke, R. Valiullin,* Leipzig University, Germany

Elaborate determination of the pore structure of mesoporous solids offers important guidance towards optimal design of various applications such as catalysis, molecular separations and adsorption, among others. Routinely used characterization tools, such as gas sorption, typically utilize the general adsorption isotherm (GAI) equation derived for ordered pore systems. Te complex morphology of disordered porous solids, with its resulting cooperativity effects in thermodynamic phase transitions, renders characterization more complex than what the GAI provides.

In this work, we present a recently developed serially connected pore model (SCPM), which extends the by incorporating cooperativity effects in phase transitions arising from pore complexity. Modeled as statistically disordered linear chain of pores, the SCPM will be validated with data from phase transitions in a synthesized porous silica material of similar pore construct, MCM-41. As an analogue to gas sorption (adsorption/desorption) studies, solid-liquid phase transitions (freezing/melting) of water in porous materials will be employed to correlate with the theoretical model and to reveal geometric disorder in SBA-15 material.

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Application of the serially connected

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SS-Contributed On Demand-10 Electrical Resistance Response of a Zno Single-Crystalline Substrate to Trace Ethanol Under Pulsed Air Jet Irradiation*, **Taku Suzuki**, Y. Adachi, T. Ohgaki, I. Sakaguchi,* National Institute for Materials Science, Japan*; M. Nakamura, H. Ohashi, A. Aimi, K. Fujimoto,* Tokyo University of Science, Japan

The pulsed jet technique was applied to measure the electrical resistance response of a Zn-terminated ZnO(0001) substrate to trace ethanol in the air to simulate the realistic working surface of a semiconductor gas sensor in a vacuum. The resistance response to the trace ethanol under the static atmospheric pressure air was well reproduced by the periodic pulsed jet technique with the optimal irradiation conditions, in which the pressure in the vicinity of the surface transiently reached 2 kPa. The behavior of the resistance upon the pulsed jet irradiation was discussed in terms of the ionsorption of oxygen. Because the background pressure was kept low enough during the pulsed jet irradiation, the reaction products during the ethanol sensing, such as acetaldehyde, has been successfully detected at the elevated temperature above 400 K by temperature programmed desorption-mass spectrometry (TPD-MS).

SS-Contributed On Demand-13 Elucidate 3D Structure of PM2.5 Aerosol Particles using ToF-SIMS*, **Zihua Zhu**, Y. Zhou,* Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, WA, 99354, USA*; F. Mei,* Atmospheric Science and Global Change Division, Pacific Northwest National Laboratory, Richland, WA, 99354, USA

The primary and secondary particles are the main sources compose of the atmospheric aerosols. Primary emissions, such as biogenic emission, biomass burning, and vehicle exhausts, not only provide primary particles to the atmosphere but also supply precursors for the formation of secondary aerosol (SA). Many analysis tools have been used to study chemical components of SA, elucidating that SA is made up of complex components. However, most of the analysis tools only analyze the aerosol bulk properties, lack of capabilities to provide necessary information to elucidate the particles’ two-dimensional (2D) and three-dimensional (3D) structure. Such information is critical in many aerosol models, because it can be used to distinguish homogeneous and heterogeneous reactions. Time-of-flight secondary ion mass spectrometry (ToF-SIMS) is a powerful surface analysis tool with several unique advantages. For example, it can provide elemental, isotopic and molecular information simultaneously. Also, its information depth is very shallow (typically 1-3 nm), and surface-specific information can be collected. In addition, it has excellent sensitivity (ppm level) and an excellent spatial resolution (sub-micron). In this research, we used ToF-SIMS to study PM2.5 SA particles collected in a typical Beijing winter pollution case in 2019. Combined with traditional scanning electron microscope and bulk analysis data, the 3D structure of aerosol particles under different pollution conditions was determined. Our results provide critical information to improve current aerosol formation models.

SS-Contributed On Demand-16 Facet-Dependent Study of the Interaction of Water Vapor With Fe_2O_3 at Near Ambient Conditions*, **Nabajit Lahiri**, D. Song, M. Zong, X. Huang, X. Zhang,* Pacific Northwest National Laboratory*; K. Stoerzinger, P. Adiga, Q. Carvalho,* Oregon State University*; M. Blum,* Lawrence Berkeley National Laboratory*; K. Rosso,* Pacific Northwest National Laboratory

Hydroxylation and wetting of iron oxide surfaces are one of the most ubiquitous processes occurring in nature as well as in technological systems. However, probing such a phenomenon in-situ under ambient conditions tend to be extremely challenging. Here, we present our recent developments using ambient-pressure X-ray photoelectron spectroscopy (AP-XPS) in conjunction with density functional theory (DFT) calculations, to probe the facet-dependent interaction of molecular water vapor on hematite nanoparticles. Size- and morphology-controlled synthesis were conducted to generate hematite nanocrystals with specific facets exposed, namely, (001), (012), and (104). The physisorption of molecular water and subsequent formation of hydroxyl species on the surface of hematite was then monitored in-situ using the O 1s photoelectron spectra acquired over a range of water vapor pressures (10^{-9} Torr < $p(H_2O)$ < 0.1 Torr). The results clearly reveal that the exposed crystallographic facet has a dramatic impact on the hydroxylation and wettability of the hematite surface.Although the onset of hydroxylation for the three surfaces occur at similar relative humidity values of about 10^{-7} Torr, the (104) facet was seen to undergo significantly higher net surface hydroxylation when compared to the (012) and (001) facets. The present study greatly advances our knowledge of the interaction of water with hematite and paves the way for the rational design of better photocatalysts for solar water splitting applications. Furthermore, such studies are essential for gaining deeper insight into various natural processes including, iron-mediated mobility of inorganic and organic pollutants in soil, nitrogen fixation, and corrosion, to name a few.

SS-Contributed On Demand-19 Influence of Geometric Disorder on Fluid Phase Transitions in Disordered Mesoporous Solids*, Henry R. N. B. Enninful, D. Schneider, D. Enke, R. Valiullin,* Leipzig University, Germany

Majority of porous solids used in industrial processes such as energy storage, separations and catalysis possess structural disorder over varying length scales. These disorder effects strongly affect the properties of the confining fluids in the pores. Hence, detailed quantification of structural disorder with correlation to fluid phase behavior is a necessary step towards optimization for practical applications.

Employing the serially connected pore model, (SCPM), we have determined the impact of a number of disorder-related parameters, including effect of pore chain length, "powder effect" and inter-connectivity effect on phase transitions in disordered mesopore spaces. Additionally, we have showed experimental results from solid-liquid phase transitions obtained by NMR cryoporometry and gas-liquid transitions observed from nitrogen sorption experiments to corroborate the theoretical predictions from the SCPM.

We conclude that, the SCPM has the potential of explaining many features of experimentally observed phase transitions in disordered mesoporous solids.

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SS-Contributed On Demand-22 Use of Ultra Thin Atomic Layer Deposited Capping Layers to Increase Stability in Thermally Processed Metalcone Thin Films*, Vamseedhara Vemuri,* *N. Strandwitz,* Lehigh University

Molecular layer deposition (MLD) and atomic layer deposition (ALD) are sequential, self limiting thin film deposition techniques, used to fabricate organic, inorganic, and inorganic-organic hybrid thin films. The hybrid organic-inorganic films deposited using MLD are usually metal alkoxides that are also termed as metalcones. Metalcone films can be subjected to thermal processing to selectively remove the organic parts of the film and induce porosity. However the as deposited and thermally processed metalcone films are unstable in ambient atmosphere due to the moisture absorption and permeation, which alters the chemical properties of these films. Since the dielectric constant of the water is very high (70-80), the net dielectric constant of these films increases after moisture absorption thus affecting the electrical properties. To preserve the chemical stability and electrical properties of metalcones, this work examines the use of an ultra thin ALD film grown over the as deposited and thermally processed films.

We report the growth of alucone thin films using trimethylaluminum and ethylene glycol as precursors for MLD and water (H_2O) as an oxygen source for ALD reactions. The as deposited MLD films are subjected to thermal processing from 150-350˚C in inert atmosphere and under UV light to remove the organic components and induce porosity. We examined the thermally induced changes in film's chemistry, thickness, density, etch rate and dielectric constant.

Incorporation of the organic components, formation of M-O-C bonding and water absorption is confirmed using FTIR in the as deposited MLD films. By subjecting MLD films to thermal processing the decrease in intensity of hydrocarbon bonds and changes in thickness, density compared to pure MLD films can be observed by FTIR and x-ray reflectivity respectively. The dielectric constant of these films is measured using capacitance-voltage measurements. The dielectric constant of the thermally processed films with a thin ALD layer decreases compared to only thermally processed films indicating that the thin ALD layer thus preserves electrical properties of the film. The as deposited and thermally processed films with and without the ultrathin ALD layer are subjected to CF_4/O_2 plasma etch and the MLD films without an ALD layer shows more than double the etch rate compared to the MLD films with an ALD layer. Both the decreased dielectric contant and etch rates show that the ALD layer acts as a barrier to prevent moisture absorption and preserve the chemical stability and electrical properties of the film.

SS-Contributed On Demand-25 In-Situ Visualization of Surface Plasmon-Driven Hot Carrier Generation With Photoconductive AFM*, Hyunhwa Lee,* *K. Song,* Institute for Basic Science (IBS), Korea (Republic of)*; M. Lee,* Inha University, Korea (Republic of)*; J. Park,* Institute for Basic Science (IBS), Korea (Republic of)

Understanding the inter-coupling between surface plasmon and the electronic distribution in metallic nanostructures is a challenging topic to develop applications of plasmonic solar-cells and efficient photodetectors. Non-radiative surface plasmon decay produces highly energetic electron-hole pairs on the metal surface with desirable characteristics.[1] Since these carriers, called hot electron/or hot hole, dissipate their energies within the femtosecond resolution, it is hard to directly observe the fast-delivering during photocatalytic reaction. Thus, research on identifying surface plasmon-driven hot carrier dynamics at the nanoscale is of great importance. Here, we demonstrate the direct observation of surface plasmon-driven hot carriers created in a Schottky platform using photoconductive atomic force microscopy (pc-AFM).[2-3] We fabricated Au nanoprism on n-type TiO_2 film and p-type GaN substrate for detection surface plasmon-driven hot electron and hot holes, respectively. We show significant enhancement of photocurrent in the plasmonic platforms under light irradiation, providing direct evidence of plasmonic hot carrier generation. Experimental and numerical analysis verified that a confined |E|-field surrounding a single Au nanoprism spurred resonant coupling between localized surface plasmon resonance (LSPR) and surface charges, thus boosting hot carrier generation. Furthermore, geometrical and size dependence on the extraction of LSPR-driven hot carriers suggests an optimized pathway for their efficient utilization. The direct visualization of hot carrier flow at the nanoscale provides significant opportunities for harnessing the underlying nature and potential of plasmonic hot carriers.

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SS-Contributed On Demand-28 Impact of Hot Hole Transport on Photocatalytic Activity in Au Nanoprisms/p-Gan under Water Splitting Reaction*, Kyoungjae Song,* Korea Advanced Institute of Science and Technology (KAIST) & Institute for Basic Science (IBS), Korea (Republic of)*; H. Lee,* Institute for Basic Science (IBS), Korea (Republic of)*; M. Lee,* Inha university, Korea (Republic of)*; J. Park,* Korea Advanced Institute of Science and Technology (KAIST) & Institute for Basic Science (IBS), Korea (Republic of)

Under the irradiation of light, excited carriers with high kinetic energy (1-3 eV) can be generated in plasmonic metals. The carriers consist of hot electrons and hot holes. The hot holes have a considerable potential due to their more energetic kinetics relative to hot electrons. To utilize hot holes by localized surface plasmon resonance, a plasmonic metal/ p-type semiconductor Schottky platform was proposed. Utilizing Au nanoparticle/ p-GaN photocathode, hot holes can be detected and photocatalytic reaction by hot holes can also be measured.

To investigate the correlation between photocatalytic activity and hot holes by surface plasmon, we fabricated size-controlled Au nanoprisms/ p-GaN photocathode using an e-beam evaporator. The electrical properties of the platform were measured by the conductive atomic force microscopy and Kelvin probe force microscopy. The triangle-shaped Au has a thickness of 10 nm and a length of 90 nm, 140 nm, and 220 nm. The small-sized Au nanoprism exhibited a high external quantum efficiency by a factor of 2 compared to that of the large one. We found that the amount of hydrogen and oxygen gas evolution increased as the size of Au nanoprism decreased from 220 nm to 90 nm. The results indicate the enhanced hot hole flux by amplification of localized surface plasmon resonance leads to the promotion of hydrogen and oxygen gas evolution reaction.

SS-Contributed On Demand-31 Observation of Atomic-scale Gliding Effect on Hydrophilic Surfaces at High Humidity*, Tae Won Go,* Korea Advanced Institute of Science and Technology (KAIST) & Institute for Basic Science (IBS), Korea (Republic of)*; H. Lee, J. Kim,* Institute for Basic Science (IBS), Korea (Republic of)*; D. Lee, J. Park,* Korea Advanced Institute of Science and Technology (KAIST) & Institute for Basic Science (IBS), Korea (Republic of)

Most semiconductors in modern industries consist of hydrophilic surfaces, which play a crucial role in the performance of nano-electromechanical systems (NEMS). The nanoscale friction behavior of adsorbed water layers on hydrophilic surfaces includingsilica and mica with exfoliated graphene was investigated by friction force microscopy (FFM) in various relative humidity (RH) conditions. Depending on the RH, the change in the topography and friction of surfaces could be observed. The friction on both of mica and silica initially increased with respect to RH and started to decrease at an intermediate RH (~ 70%). At high RH (> 98%), the height of graphene and silica were non-distinguishable, and graphene showed higher friction than silica. In addition, the water intercalation between graphene and hydrophilic surfaces formed subdomain structure within graphene sheet, which showed enhanced friction due to more efficient energy dissipation mediated by electron-phonon interaction. These results suggest that the abundance of adsorbed water molecules at probe/hydrophilic surface interface lead to atomic-scale gliding that overcomes capillary and viscosity effects. The finding may provide useful insights for semiconductor applications in ambient conditions.

SS-Contributed On Demand-34 Pt/Ag/TiO_2 Plasmonic Nanodiode for Extraction of Surface Plasmon-Driven Chemicurrent*, Mincheol Kang,* *B. Jeon, Y. Park,* Korea Advanced Institute of Science and Technology (KAIST) & Institute for Basic Science (IBS), Korea (Republic of)*; H. Lee,* Institute for Basic Science (IBS) , Korea (Republic of)*; J. Park,* Korea Advanced Institute of Science and Technology (KAIST) & Institute for Basic Science (IBS), Korea (Republic of)

Solar energy conversion to improve catalytic performance is actively studied, and the design of photocatalysis incorporating surface plasmon is drawing significant attention as a highly competitive catalyst system. Important factors of surface plasmon are size, shape, and material of plasmonic metal nanostructures, which affect plasmonic excitation, absorbance, and hot electron collection.In this study, we fabricated Schottky nanodiodes with nanoscale Pt/Ag patterns with controlled size and shape using nanosphere lithography and reactive ion etching. Plasmonic nanodiodes composed of Pt/Ag/TiO_2 were used to detect exothermic surface reaction-induced hot electrons under hydrogen oxidation. In this system, the surface temperature was measured using the thermovision to distinguish contributions of the plasmonic effect and the photothermal heating effect. When the light of the particular wavelength region (400~500 nm) is incident on the diodes, both chemicurrent and catalytic activity of hydrogen oxidation were amplified by the plasmonic effect of antenna Ag. In addition, we show the visualization of the plasmonic effect using the finite difference time domain simulations. The novel scheme of antenna-reactor using plamonic nanodiodes may offer a strategy for advanced hot-electron-based catalytic and photovoltaic devices.

SS-Contributed On Demand-37 Disruption of Small Alcohol Intermolecular Interactions at Defect Sites on Au(111)*, E. Maxwell, L. Garber, J. Baker, C. Rogers, H. Kaleem,* ***Ashleigh Baber,*** James Madison University

Gold-based catalysts have received great study as supports and nanoparticles for heterogeneous catalysis in recent years, in part due to the ability of Au to catalyze reactions at low temperatures in oxidative environments. Surface defects are known as active sites for low temperature chemistry on Au surfaces, so a full understanding of the interplay between intermolecular interactions and surface morphology is essential to an advanced understanding of catalytic behavior and efficiency. In a systematic study to better understand the adsorption and intermolecular behavior of small alcohols (C_1-C_4) on Au(111) defect sites, coverage studies of methanol, ethanol, 1-propanol, 1-butanol, and 2-butanol have been conducted on Au(111) using ultrahigh vacuum temperature-programmed desorption (TPD). These alcohols molecularly adsorb on the Au(111) surface, and high resolution experiments reveal distinct terrace, step edge, and kink adsorption features for each molecule. The hydrogen-bonded (H-bonded) networks of these small alcohols on Au(111), except 1-butanol, have been previously imaged on the molecular level at low temperatures by ultrahigh vacuum scanning tunneling microscopy (UHV-STM). Primary alcohols up to 1-propanol exhibit planar H-bonded zigzag chain networks while 2-butanol arranges in tetramer clusters of H-bonded molecules due to steric hindrance inhibiting the proximity of molecules on Au(111). Interestingly, the adsorption, desorption, and molecular structure of 1-butanol on Au(111) has yet to be investigated. In this study, the desorption energy of small primary alcohols was shown to trend linearly with increasing carbon chain length through the range of C_1-C_4, indicating that the H-bonded molecular packing of 1-butanol resembles that of methanol, ethanol, and 1-propanol. The distinction between the desorption of 1- and 2- butanol highlights the role of intermolecular interactions due to the difference in molecular packing structures on Au(111). Furthermore, by studying the energetics of terrace H-bonded networks in comparison with molecular adsorption to undercoordinated step edge and kink defect sites, it is shown that the contribution of stabilizing intermolecular interactions and van der Waals (vdW) forces to the overall adsorption energy is less for small alcohols adsorbed at kink sites and similar for those adsorbed at step edge sites relative to alcohols adsorbed on the Au terrace.

SS-Contributed On Demand-40 Interaction of Amino Acids on Au(111) as Studied with EC-STM: From Islands to Magic Fingers*, K. P. S. Boyd, E. Cook, M. Paszkowiak,* ***Erin Iski,*** The University of Tulsa

With growing interest into origin of life studies as well as the advancement of medical research using nanostructured architectures, investigations into amino acid interactions have increased heavily in the field of surface science. Amino acid assembly on metallic surfaces is typically investigated with Scanning Tunneling Microscopy (STM) at low temperatures (LT) and under ultra-high vacuum (UHV), which can achieve the necessary resolution to study detailed molecular interactions and chiral templating. However, in only studying these systems at LT and UHV, results often tend to be uncertain when moving to more relevant temperatures and pressures. This investigation focuses on the Electrochemical STM (EC-STM) study of five simple amino acids (L-Valine, L-threonine, L-Isoleucine, L-Phenylalanine, and L-Tyrosine) as well as two modifications of a single amino acid (L-Isoleucine Ethyl Ester and N-Boc-L-Isoleucine), and the means by which these molecules interact with a Au(111) surface. Using EC-STM under relevant experimental conditions, the amino acids were shown to have a considerable interaction with the underlying surface. In some cases, the amino acids trapped diffusing adatoms to form Au islands and in other cases, they assisted in the formation of magic gold fingers. Importantly, these findings have also been observed under UHV conditions, but this is the first demonstration of the correlation *in situ* and was controlled via an external applied potential. Results indicate that an increase in the molecular weight of the amino acid had a subsequent increase in the area of the islands formed. Additional studies examining the role that surface temperature played in the formation of the adatom islands will also be discussed. By analyzing the results gathered via EC-STM at ambient conditions, fundamental insight can be gained into not only the behavior of these amino acids with varied side chains and the underlying surface, but also into the relevance of LT-UHV STM data as it compares to data taken in more realistic scenarios.

SS-Contributed On Demand-43 Resonant ARPES Reveals the Origin of the 2DEG in $SrTiO_3$ and $SriTiO_3$ Heterostructure*, Jessica McChesney,*** *X. Yan, H. Hong, D. Fong,* Argonne National Laboratory

The origin of the two dimensional electron gas/liquid (2DEG) at the surface of bare $SrTiO_3$ and $SrTiO_3$-based heterostructures has been under debate since it was first observed in $SrTiO_3$/$LaAlO_3$. This debate is largely fueled by the ubiquity of the 2DEG from often seemingly contradictory conditions. For instance, the 2DEG has been both observed and not observed for freshly cleaved SrTiO3, or in-vacuum annealed $SrTiO_3$ wafers, argon-sputtered surfaces, and for various heterostructures where a minimum overlayer thickness is required. Using resonant angle-resolved photoemission spectroscopy, we show that it is not oxygen defects that are the requirement for the formation of the 2DEG but instead any non-interacting electron donor, including those produced as part of the photoemission process that can induce sufficient band bending for forming the quantum well 2DEG.

SS-Contributed On Demand-46 Self-selective Formation of Organized 1D and 2D GaBi Structures on Crystal-phase Modulated GaAs Nanowires*, Yi Liu,*** *R. Timm, S. Benter,* Lund University, Sweden*; E. Young,* University of California at Santa Barbara*; S. Lehmann, K. Dick,* Lund University, Sweden*; C. Palmstrøm,* University of California at Santa Barbara*; A. Mikkelsen,* Lund University, Sweden

Yi Liu[1], Sandra Benter [1] , Elliot Young[2], Sebastian Lehmann[1], Kimberly A. Dick[3], Chris J. Palmstrøm[2], Anders Mikkelsen[1], and Rainer Timm[1]

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Semiconductor devices made up of only a few atoms in size with precise positions have been highly challenging but are crucial for new applications in quantum computing and sensing. III-V semiconductor nanowires (NWs) have the merit of controllable axial stacking of different crystal phases with exposing different crystal facets, which is ideal for studying surface functionalization at the nano scale. Bismuth (Bi) incorporation and alloying in III-V semiconductors such as InAsBi and GaAsBi have become popular due to a number of promising properties, such as predicted band inversion and topological behavior in the case of high Bi concentrations. However, the realization of alloys with high Bi content by epitaxial growth has remained challenging, and GaBi bonds have been considered to be unstable.

We use the sidewall facets of NWs with both zinc blende (Zb) and wurtzite (Wz) segments as templates, and study self-selective growth under Bi deposition by low-temperature scanning tunneling microscopy and spectroscopy (STM/S). We observe the site-selective Bi incorporation on the surface via the Bi-for-As exchange reaction. More specifically, we find a crystal structure dependent surface alloying process, where ordered GaBi structures such as 2D islands and 1D atomic chains of a few atoms are formed on Wz {11-20} facets, while randomly distributed single Bi sites are found on Zb {110} facets. This self-selective formation process of ordered GaBi nanostructures is attributed to different diffusion barriers and surface geometries of the different surface facets. Lastly, signs of a length-dependent energy confinement effect in Bi-chains are observed via STS, which also indicates a smaller band gap on the surface of GaBi islands made up of a few tens of atoms on GaAs NWs. X-ray photoelectron spectroscopy with nanoscale beam size has also been used to evaluate chemical states before and after Bi incorporation.

Our results indicate a promising way to realize versatile high precision design of device structures with controllably positioning of materials at the atomic scale, by utilizing tailored NW heterostructure and surface facet variations.

SS-Contributed On Demand-49 Growth and Morphology of Well-ordered Metal Doped-CeO$_x$(111) Interfaces, *L. Du, E. Ginting,* ***Jing Zhou,*** Department of Chemistry, University of Wyoming

Ceria has been widely studied as an oxidation-reduction catalyst due to its unique redox properties and oxygen storage capacity [1]. Doping ceria with additional metal elements can enhance its thermal stability. The interaction of metal dopants with ceria can also lower the activation energy needed for the release of oxygen, which can result in the improvement of its redox properties and oxygen storage capacity and consequently the enhancement of its catalytic activity. To understand the chemistry of doped-ceria mixed oxides, it is of crucial importance to determine their surface structures at the fundamental level. We present our study on the growth of ceria thin films with Ti and Mn dopants and the understanding of their structures using X-ray photoelectron spectroscopy, low-energy electron diffraction, as well as scanning tunneling microscopy under ultrahigh vacuum conditions. In our study, well-ordered CeO$_x$(111) (1.5 <x<2) thin films with controlled degree of Ce reduction and atomic structures were grown on a Ru(0001) single crystal substrate [2]. Metal-doped ceria mixed oxide interfaces were prepared by depositing Ti or Mn over CeO$_x$(111) thin films. Co-deposition of Ce with metal dopants during the film growth can produce well-ordered Ce$_{1-y}$M$_y$O$_x$(111) (M=Ti, Mn) mixed oxide films [3]. Our data show that dopant types and growth conditions can influence the surface structures, electronic and redox properties of ceria. Effects of Mn and Ti dopants in ceria were further investigated for supported Ni. Compared to pure ceria, addition of metal dopants in ceria can provide unique anchoring sites and interaction for deposited Ni, which can significantly stabilize Ni as small metal nanoparticles upon heating. The chemical state of Ni is dependent on the nature of the ceria support. Modified structures and electronic properties of ceria by dopants provide promotional effects in the activity and stability of Ni nanoparticles in the dry reforming of methane reaction. The research is sponsored by the National Science Foundation Grant (Award Number: CHE1151846) and Wyoming Carbon Engineering Initiative from School of Energy Resources at University of Wyoming.

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SS-Contributed On Demand-52 STM and XPS Studies of Co Nanoparticles on Reducible CeO$_2$(111) Thin Films, ***Jing Zhou,*** *L. Du,* University of Wyoming

STM and XPS Studies of Co Nanoparticles on Reducible CeO$_2$(111) Thin Films

Linze Du and Jing Zhou*

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Cobalt metal catalysts have been of great interest as economical and promising catalysts for ethanol reforming and dry reforming of methane reactions. Ceria can be a suitable choice as the catalytic support for Co since unique redox properties and oxygen storage capacities of ceria can influence the size, structure, chemical state, and thus the catalytic performance of Co. To elucidate the nature of the reactivity, it is of significance to gain a fundamental understanding of the structure and electronic properties of Co particles on ceria supports. Here we report our studies of Co deposited on fully oxidized CeO$_2$(111) and reduced CeO$_x$(111) thin films using scanning tunneling microscopy and X-ray photoelectron spectroscopy. Ceria thin films were grown in situ on Ru(0001) under ultrahigh vacuum conditions. The growth of Co particles was investigated as a function of Co coverages, deposition temperatures, post-deposition annealing temperatures, as well as degrees of Ce reduction. At 300 K, oxidation of Co to Co^{2+} occurs on fully oxidized CeO$_2$. At low Co coverages (<0.2 ML), Co^{2+} is the predominant species. With the increase of the Co coverage, both metallic and Co^{2+} species can be present on CeO$_2$. Metallic Co is the major species formed on partially reduced ceria. Co forms two-dimensional small particles on ceria at room temperature. With further heating to 1000 K, the particles can agglomerate into three-dimensional structures. However, they are on average less than 1 nm high at 1000 K. A comparison of the growth of Co on CeO$_2$(111) with our previous studies of Au, Ni, Pt, and Rh at the same coverage demonstrates that Co forms the smallest clusters, which suggests a stronger Co-ceria interaction. Our study presents model Co-ceria catalytic systems for further investigation of the chemistry in the reforming process related with particle sizes, chemical states and support effects. The research was sponsored by the National Science Foundation Career Grant (Award Number: CHE1151846) and Wyoming Carbon Engineering Initiative from School of Energy Resources at University of Wyoming.

SS-Contributed On Demand-55 Electronic Structure of a Carbon Dot Monolayer on TiO$_2$(110), ***Jan Eric Beckord,*** *M. Hengsberger,* University of Zurich, Switzerland; *A. Cannizzo,* University of Bern, Switzerland; *J. Osterwalder,* University of Zurich, Switzerland

Carbon dots are nanometer-sized particles with a carbon core and a functionalized organic shell. Our research focuses on their photocatalytic properties: for example, the oxygen evolution reaction at titanium dioxide surfaces under visible light irradiation is significantly improved [1]. To elucidate the electronic structure and dynamics of this system, we adsorbed a single layer of carbon dots with an average size of 4 nm on a clean rutile TiO$_2$(110) surface from aqueous solution under vacuum. Our XPS measurements revealed a coverage of approximately one monolayer, an increased upward band bending of the n-doped substrate and a lowered work function. A continuum of additional occupied and unoccupied states is found using ultraviolet photoemission spectroscopy (UPS) and two-photon photoemission spectroscopy (2PPE) due to the various molecular orbitals on the carbon dots. The analysis of 2PPE measurements at different photon energies does not reveal any resonant transitions which would result in an increased intensity. Optical absorption and fluorescence measurements of the carbon dots in aqueous solution support this claim, as the typical broad absorption and excitation-dependent fluorescence of carbon dots with such an electronic structure are observed [2]. These continua of electronic states facilitate exciton generation from visible light, explaining the function of carbon dots as effective photosensitizers. The excited electrons are then efficiently transported to the substrate, as the band alignment forms a p-n-junction at the interface. We show this with time-resolved 2PPE, where the observed transfer time according to our interpretation is in the femtosecond range, much faster than the relaxation time of 6 ns previously measured with time-resolved fluorescence spectrometry in aqueous solution [3]. We conclude that carbon dots donate excited electrons to the substrate, leaving catalytically active holes behind. Additionally, we found excellent long-term stability even in ambient air and under strong light, making this system suitable for applications under ambient conditions.

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SS-Contributed On Demand-58 UHV Growth and Characterization of Ga_2O_3 on Cu_2O (111)*, **Mert Taskin**, T. Kälin, C. Hanisch, J. Osterwalder,* University of Zurich, Switzerland

Photoelectrochemical cells have been attracted more and more attention in recent years because they are promising candidates to store clean and renewable solar energy in chemical form. Cu_2O, a natural p-type semiconductor with a direct bandgap of 2.17 eV, has a conventional conduction band position slightly above the water reduction potential and offers a low-cost photocathode for unassisted water splitting devices [1]. However, bare Cu_2O lacks photovoltage under illumination. Overlayers of n-type Ga_2O_3 can be employed to reduce the interfacial recombination effects due to the adequate conduction band alignment with Cu_2O, leading to an increase in photovoltage [2]. In this work we investigate the electronic properties and the morphology of surfaces and interfaces of UHV-grown Ga_2O_3 on Cu_2O(111) with surface science methodology. In particular, we study the effect of post-annealing treatments and the influence of a reconstruction of the Cu_2O(111) substrate prior to Ga_2O_3 deposition.

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SS-Contributed On Demand-61 Tracking the Ultrafast Dynamics of Surface Photoinduced Reactions on Amorphous Surfaces With With Time, Mass, and Energy Resolution*, **Mihai Vaida**,* University of Central Florida

In surface-aligned-reactions (SAR), reagent species produced by the photolysis of aligned molecules adsorbed on crystalline solids tend to move in well-defined directions relative to the crystal surface. In this case, the degrees of freedom of surface chemical reactions are restricted, and therefore the reaction outcome is in general predictable. In contrast to SAR, on amorphous surfaces, molecules can have various adsorption geometries and therefore their reaction outcome is unforeseeable. In this work, to understand the effect of random molecular adsorption geometries on the surface reaction, the ultrafast photoinduced reaction dynamics of the deuterated methyl iodide (CD_3I) molecules adsorbed on amorphous cerium oxide films is investigated. An experimental technique that combines surface mass spectrometry with femtosecond pump excitation-dissociation followed by probe ionization-detection in employed. This technique can be used to decipher the complex surface reaction dynamics through detection of reaction intermediates and final products with time-, mass-, and energy resolution. A minimum dissociation time of 126 fs is measured after the A-band excitation of the CD_3I molecules. The faster gas-phase release of CD_3 relative to I, indicates that the CD_3I molecules are predominantly connected to the surface through the iodine atom. After the dissociation, the fragments are not produced at a steady rate, decaying as a function of the pump-probe time delay, which indicates a further surface reaction. The decay time of I (8 ± 0.5 ps) is similar to the release time of I_2(8.5 ± 0.3 ps), while the decay time of CD_3 (2.5 ± 0.3 ps) is similar to the release time of the CD_3I (2.2 ± 0.3 ps) molecules that are reformed on the surface. Interestingly, no I_2 or CD_3I molecules are detected within the first 800 fs after the initial excitation. This is due to the high kinetic energy with which the fragments are released after dissociation. This energy is lost through collisions with the surface or neighboring adsorbates to facilitate the bimolecular reaction, as reveled by monitoring the time-of-flight of the mass peaks as a function of the pump-probe time delay.

SS-Contributed On Demand-64 Investigating the Effect of Sn Vapor Deposition Parameters on Nb-Sn-O Coordination on a Highly-Ordered Oxidized Nb(100) Substrate*, **Sarah Willson**, R. Farber, S. Sibener,* University of Chicago

Niobium is the current standard elemental material for superconducting radiofrequency (SRF) cavities, but is limited to operating temperatures of ~ 2 K. To achieve improved accelerating gradients at increased operating temperatures (> 4 K), efforts are underway to coat Nb SRF cavities with Nb_3Sn thin films. However, the accelerating performance of Nb_3Sn coatings fabricated using the vapor deposition procedure is limited by the surface roughness and presence of near-surface defects such as atomic dislocations, inhomogeneities, and high grain boundary densities. This experimental study aims to identify the relationships between Nb_3Sn growth parameters such as the Sn flux, Nb oxide content, Nb defect density, and annealing temperatures both during and post-deposition on the resultant Nb-Sn-O surface interactions that dictate alloy morphology.

Using a well-characterized (3×1)-O/Nb(100) single crystal, Sn deposition was done 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. To induce alloy formation, the (3×1)-O/Nb(100) surface was exposed to precise monolayer equivalences of Sn (10.0 - 20.0 ML) and subsequently annealed between 500 – 1000 °C. Results suggest that the substrate deposition temperature and Nb oxide morphology are two of the most significant factors affecting both the persistence of Sn on the Nb substrate as well as Nb-Sn-O oxidation behavior. AES data demonstrate that Sn deposition on an 800 °C substrate suppresses Sn desorption during 800 - 1000 °C post-deposition anneals. Furthermore, XPS data distinguish the relationship between the oxidation state of Sn adlayer contributions and the resultant Sn desorption behavior. Ongoing experimental studies aim to demonstrate the impact of altering numerous vapor deposition conditions on the growth mechanisms and alloying dynamics that ultimately enable pristine Nb_3Sn growth.

SS-Contributed On Demand-67 Reactions of Boron-containing Molecules with H- and Cl-terminated Si(100)*, **Dhamelyz Silva Quinones**, A. Teplyakov,* University of Delaware*; R. Butera,* Laboratory for Physical Sciences*; G. Wang,* Sandia National Laboratories

The reactions of boron trichloride, boric acid and 4-fluorophenylboronic acid in solution were studied in order to understand the interaction of these molecules with hydrogen- and chlorine terminated Si(100) surfaces prepared in solution. The reactions were mainly followed by X-ray photoelectron spectroscopy (XPS) which shows that these molecules react preferentially with Cl-Si(100) compared with H-Si(100) at similar conditions. Within the range of reaction conditions investigated, boron trichloride reacts preferentially with the Cl-terminated surface compared to H-terminated surface. On this Cl-Si(100) surface, the direct Si-B direct bond is formed as confirmed by XPS. At 70°C, the reaction loses its selectivity and both surfaces form B-containing surface species. Boric acid and 4-fluorophenylboronic acids react selectively with Cl-Si(100) surface, introducing boron onto the surface and forming a Si-O-B structure. The quantification of boron surface coverage demonstrates that the 4-fluorophenylboronic acid leads to ~3 times higher boron coverage compared to boric acid on Cl-Si(100). Density functional theory was utilized to identify possible major surface species resulting from these reactions and to supplement the experimental findings, showing that the reactions of boric acid and 4-fluorophenylboronic acid are more favorable with the Cl- versus H- terminated surface, and on Cl-Si(100) the reaction with 4-fluorophenylboronic acid is more thermodynamically favorable than the reaction with boric acid. This work provides a new pathway to obtain a functionalized silicon surface with a direct Si-B bond and boron incorporation into silicon surface via Si-O-B bonds that can be used for further functionalization or as a means of selective-area monolayer doping.

SS-Contributed On Demand-70 2020 AVS Dorothy M. and Earl S. Hoffman Scholarship Award Talk: Ru Precursors for Photoassisted Chemical Vapor Deposition: Comparison of Allyl and Diene Complexes*, **Christopher Brewer**[1], N. Sheehan,* University of Florida*; B. Salazar,* University of Texas at Dallas*; J. Herrera,* University of Florida*; A. Walker,* University of Texas at Dallas*; L. McElwee-White,* University of Florida

Chemical vapor deposition (CVD) is a potentially attractive technique for the metallization of organic thin films. However, thermal CVD processes often require high temperatures which are incompatible with organic

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[1] **AVS 2020 Dorothy M. and Earl S. Hoffman Scholarship Awardee**

substrates. Photochemistry provides an alternative means of initiating precursor decomposition without heating the substrate. Readily available Ru precursors, such as $(\eta^3\text{-allyl})Ru(CO)_3X$ (X = Cl, Br, I), have been used to deposit Ru on functionalized self-assembled monolayers by means of photochemical CVD as a model system for deposition of metal on a thermally sensitive substrate. Quantum yields for loss of a single CO ligand in alkane solutions were determined for the $(\eta^3\text{-allyl})Ru(CO)_3X$ complexes, to elucidate the photochemistry that initiates the deposition process. As a comparative study, the quantum yields for various $(diene)Ru(CO)_3$ complexes were determined. These $(diene)Ru(CO)_3$ undergo mixed photolytic decomposition pathways, making them attractive precursors for photochemical CVD. This talk will discuss the photochemistry of the $(diene)Ru(CO)_3$ complexes relative to the $(\eta^3\text{-allyl})Ru(CO)_3X$ complexes with respect to their deposition results.

SS-Contributed On Demand-73 Thermal Atomic Layer Etching of CoFeB Alloy Thin Films Using Chlorine and Acetylacetone (acacH), ***Mahsa Konh***, *A. Teplyakov,* University of Delaware

The mechanism and efficiency of thermal dry etching of CoFeB alloy thin films using Cl_2 and 2,4-pentanedione (acetylacetone, acacH) were investigated. CoFeB alloy is commonly used in magnetic random-access memory (MRAM) technology. The initial steps of etching were followed by detecting expected desorbing fragments during a linear heating ramp via temperature-programmed desorption (TPD). The chemical composition of the etched surfaces was then analyzed ex situ with X-ray photoelectron spectroscopy (XPS). The etch rate was measured by comparing the film thickness before and after ALE process using atomic force microscopy (AFM) of patterned samples. The overall mechanism of thermal etching on the alloy thin films is quite complicated as the desorbing metal-containing products have the overall formula $M(acac)_xCl_y$; however, it appears that the process does not affect the surface concentrations of the alloy constituents.

SS-Contributed On Demand-76 Following the Microscopic Pathways to Energy Dissipation and Adsorption in Molecule-Metal Surface Encounter, ***Igor Rahinov***, The Open University of Israel; *D. Borodin,* University of Göettingen, Germany; *P. Shirhatti,* Tata Institute of Fundamental Research, India; *M. Huang,* University of New Mexico; *A. Kandratsenka,* Max Planck Institute for Biophysical Chemistry, Germany; *D. Auerbach,* Max Planck Institute for Biophysical Chemistry; *T. Zhong,* Max Planck Institute for Biophysical Chemistry, Germany; *H. Guo,* University of New Mexico; *D. Schwarzer,* Max Planck Institute for Biophysical Chemistry, Germany; *T. KItsopoulos, A. Wodtke,* University of Göettingen, Germany

The most common mechanism of catalytic surface chemistry is that of Langmuir and Hinshelwood (LH). In the LH mechanism, reactants adsorb, thermalize with the surface and subsequently react. At the same time, molecular vibration is known to enhance the rates of gas-phase chemical reactions as the motion associated with bond stretching facilitates the reactant molecule approach to the transition state [1]. However, for reactions occurring on via LH mechanism on metal surfaces, relevant for heterogeneous catalysis reactions, the ability of vibrational excitation to promote reactivity is hampered by rapid dissipation of the vibrational energy of the reactant into electronic excitation of the metal within several picoseconds [2]. Our recent findings challenge this paradigm: we have demonstrated that excited vibrational states can survive longer than expected [3,4] – suggesting vibrational excitation might promote or modify heterogeneously catalyzed LH-chemistry on metals. In our experiments IR laser excitation was used to prepare short pulses of vibrationally excited CO(v=2) molecules that impinged and scattered from clean Au(111) surface. By quantum-state-resolved scattering studied in temporally and spatially resolved fashion we have unambiguously demonstrated that vibrationally excited molecules, prepared in the v=2 state retain significant vibrational excitation, even after residing ~ 50 ps on Au(111). Furthermore, we show that the vibrational relaxation time can serve as an internal clock to follow the microscopic pathways of adsorption and equilibration on the surface. On the basis of molecular beam experiments and theoretical modeling we reveal the intricate interplay between physisorption and chemisorption states for the prototypical CO/Au(111) system, relevant to many other heterogeneous systems.

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SS-Contributed On Demand-79 In Situ Observations of Graphene Growth on Liquid Copper, ***Irene Groot,*** Leiden University, The Netherlands

Since its first preparation a decade ago, graphene has been a promising material for many technological applications, due to its unique physical and chemical properties. However, until today graphene cannot be found yet in the devices it seems so suitable for. The reason is that the production of large sheets of defect-free graphene at time scales compatible with an industrial process has not yet been achieved. Defects in the graphene result from the grain boundaries and defects that are present at the surface of the catalyst used: solid copper. Recently, it was found that large sheets of defect-free graphene can be grown on liquid copper instead [1]. Liquid copper has a smooth surface without the defects present in solid copper, and the mobility of graphene on the liquid surface enables a fast growth process and the healing of defects. All research so far on graphene growth on liquid copper, however, has been performed after the growth and after the cooling down of the copper-graphene system to room temperature, introducing changes to the structure of graphene.

In this talk I will show the reactor that we have developed to investigate the growth kinetics of graphene on liquid copper at 1400 K *while the process is taking place*. We make use of Raman spectroscopy, optical microscopy, grazing-incidence X-ray diffraction, X-ray reflectivity and theoretical calculations to understand and tune the graphene growth. By tuning the reaction conditions during growth, we are able to grow millimeter-sized single-crystalline graphene sheets of the highest quality with a growth speed of ~ 1 micrometer/s, paving the way for their use in a range of optoelectronics applications.

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SS-Contributed On Demand-82 Laser-Photoemission Electron Microscopy —Deciphering the Morphology of Semi-Crystalline Polymer Films, ***Falk Niefind***, Physical Measurement Laboratory, National Institute of Standards and Technology (NIST); *S. Mannsfeld,* Technische Universität Dresden, Germany; *S. Karande, A. Kahnt, B. Abel,* Leibniz Institute of Surface Engineering (IOM), Germany

Reducing mankind's carbon footprint in a quest to combat climate change is one of the biggest challenges for humanity in the current century. Decarbonization of the energy sector by increasing the contribution of renewable energy sources is one vital step on this path.[1] Organic solar cells or organic photovoltaics (OPV) based on thin polymer films can play a vital role in tackling this challenge. Their appeal derives from their unique properties when compared to classical silicon-based photovoltaics: their chemical composition, mechanical properties as well as their optical characteristics can be tailored to the specifics of the area of application (e.g. walls, windows, roofs and cars).[2] However, the performance of polymer OPV devices is closely linked to the nanoscale morphology (e.g. the polymer orientation, domain size and local crystallinity) of the polymer films.[3] Thus, gaining insight into said morphology has attracted significant interest during the last decades. Traditionally, the morphology is controlled via the fabrication method such as spin coating or doctor blading as well as the fabrication parameters such as temperature, printing speed and solvents used. We present an imaging technique based on a photoemission electron microscope (PEEM) and a linearly polarized femtosecond laser system, all in tabletop format. The method can determine the polymer orientation, domain size and local degree of order in a single straight forward imaging measurement, with a spatial resolution of up to 50 nm. Our method exploits a two-photon photoemission (2PPE) process that exhibits a dichroism with respect to the linear polarization of the employed laser light and the polymer backbone. Our experiments were conducted on Poly(3-hexylthiophene-2,5-diyl) (P3HT), a benchmark polymer in the OPV community.[4,5,6]

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SS-Contributed On Demand-85 Thermal Oxidation of Ru(0001) to RuO_2 Studied With Ambient Pressure X-ray Photoelectron Spectroscopy*, J. Trey Diulus*, *Z. Novotny, B. Tobler,* University of Zurich, Switzerland*; L. Artiglia, J. Raabe,* Paul Scherrer Institute, Switzerland*; J. Osterwalder,* University of Zurich, Switzerland

Ruthenium dioxide (RuO_2) is known to be a highly efficient oxidation catalyst for heterogeneous reactions. Understanding the formation of late transition metal oxides from a fundamental approach is imperative for the heterogeneous catalysis community and can lead to improved catalyst designs.[1] Surface science literature has previously proposed from thermal desorption spectra and theory that the formation of an O-Ru-O tri-layer or RuO_x suboxides are involved in creating RuO_2, although studying the chemical state of these intermediate oxides has proven difficult.[1,2] In this study, we report on the thermal oxidation of single-crystalline Ru(0001) films *in-situ* during time-lapsed ambient pressure X-ray photoelectron spectroscopy (APXPS) measurements. As received samples were inserted into an APXPS endstation,[3] composed of a 200 nm thick Ru(0001) film deposited on a yttria-stabilized-zirconia film on top of a Si(111) substrate. Samples were treated with thermal annealing in high vacuum (HV, 10^{-7} mbar) or 0.01 mbar of oxygen and crystallinity was verified with low energy electron diffraction. During thermal oxidation, samples were exposed to a constant pressure of 0.01 mbar as the temperature was increased stepwise. At 200 ºC, we observe adventitious carbon contamination burned away, followed by a coexistence of Ru and Ru-O peaks in the Ru 3d and O 1s core levels after further heating to 300 ºC, indicating the presence of a O-Ru-O tri-layer. After 1.5 hours at 350 ºC, the metal component of the Ru 3d spectra becomes negligible and a shift in binding energy occurs in the O 1s spectra. Additionally, a satellite forms at 285 eV in between the Ru $3d_{5/2}$ and $3d_{3/2}$, characteristic of RuO_2. Furthermore, with quantitative analysis, we calculated the stoichiometry of the formed oxide film, thus providing evidence for a model pathway of the oxidation of Ru(0001).

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SS-Contributed On Demand-88 STM Study of Ag Encapsulation of Pd Islands on Ag(111)*, Buddhika Alupothe Gedara,* *M. Muir, M. Trenary,* University of Illinois at Chicago

PdAg bimetallic heterogenous catalysts play a vital role in the petroleum and chemical industries as they can enhance both activity and selectivity of hydrogenation reactions. For further development of PdAg catalysts, it is important to understand their atomic-scale behavior. We have studied Ag encapsulation of Pd islands at three different Pd coverages (0.028, 0.064, and 0.135 monolayer (ML)) on Ag(111) at room temperature (RT) using scanning tunneling microscopy. While previous studies have shown that the structure and composition of Pd islands on Ag(111) change at elevated temperatures, we found that surface Ag atoms cover the Pd islands even at RT. Our results suggest that these Ag atoms migrate to the top of the Pd islands through special defects identified as stacking fault tetrahedra (SFT), such as has been reported in previous studies on Au(111). Furthermore, we have studied the behavior of the islands upon annealing. The majority of the Pd islands are encapsulated by surface Ag atoms at 350K to form a Ag/Pd/Ag(111) structure. However, upon further annealing we observed that the composition of some islands at a 0.135 ML Pd coverage changed to Ag/Ag/Pd/Ag(111). This study reveals how surface Ag atoms migrate to encapsulate Pd islands.

SS-Contributed On Demand-91 An Xps Study of the Interaction between the Uranyl Ion and Oligoarginine Peptide*, Esha Mishra,* *C. Schultz,* University of Nebraska - Lincoln*; P. Dowben,* University of Nebraska–Lincoln*; R. Lai,* University of Nebraska - Lincoln

X-ray Photoemission Spectroscopy (XPS) was used to analyze oligoarginine polypeptide, with methylene blue on a gold substrate. The X-ray photoemission of these oligoarginine polypeptides before and after exposure to U(VI), i.e., uranous oxide, was compared. For the N 1s core level spectra, the shift of N 1s peak towards the lower binding energy was observed after the oligoarginine polypeptide was exposed to U(VI). This result suggested that there is a charge donation to the polypeptide, through the polypeptide backbone and the amine in the polypeptide is not bonding to the UO_2 oxygen, but to the uranium itself. XPS core level spectra for uranium U $4f_{7/2}$ suggested that the uranium is bonded to the oligoarginine peptide, with some back charge donation, likely related to some oligoarginine polypeptide interaction with the oxygen, to partly reduce the UO_2 moiety. We find that not all short-chain polypeptide binds effectively with U(VI), i.e., uranous oxide. This work expands XPS studies of heavy metal biomolecule interactions from interactions with deoxyribonucleic acid (DNA) to proteins and shows the utility of the technique in filling out the coordination chemistry picture.

SS-Contributed On Demand-94 Surface Stability, Phonon Band Structure, and Vibrational Dynamics of the Nb(100) Surface Oxide Reconstruction*, Alison McMillan,* *C. Thompson, J. Graham,* University of Chicago*; M. Kelley,* Cornell University*; S. Willson, R. Farber,* University of Chicago*; T. Arias,* Cornell University*; S. Sibener,* University of Chicago

Niobium's fundamental properties have led to its use in most modern superconducting radio frequency (SRF) cavities in particle accelerators, but these cavities now are approaching the performance limits of Nb. Future progress must come from the development of new materials: one promising alternative is Nb_3Sn. Nb_3Sn thin films generally are formed on bulk Nb samples, and their growth is dictated by the interaction of Sn with the Nb surface. Nb, however, has a strong affinity for oxygen; it almost always is covered by an oxide layer. An in-depth description of the oxide surface, then, is essential for improving Nb_3Sn growth procedures. This combined study, with helium atom scattering (HAS), Auger electron spectroscopy (AES), and density functional theory (DFT), investigates the microscopic structure and dynamics of the (3x1)-O surface reconstruction of Nb(100). High-resolution He diffraction and line-shape analysis, confirmed by AES, reveal that the (3x1)-O surface is stable up to at least 1130 K. The atomic-scale surface structure, composition, and coherence do not change over a wide range of temperatures, including the temperature at which Nb typically is held during Sn nucleation. Inelastic He time-of-flight measurements are used to map out the phonon band structure of the Nb(100) oxide and determine the nature of the surface vibrational dynamics. DFT calculations of the phonon band structures for both the metallic and oxidized Nb(100) surfaces show the effect of the oxide on the electronic structure and bonding at the surface and corroborate HAS data. These results impact the current understanding of the oxide covered Nb surface – critically needed information for furthering our understanding of Nb alloy formation – and aid the development of new SRF technologies.

SS-Contributed On Demand-97 Evidence of a Surface to Bulk Core Level Shift in $CoFe_2O_4$ Thin Films Grown on Al_2O_3*, Arjun Subedi,* *Y. Yun, D. Yang, X. Xu, P. Dowben,* University of Nebraska-Lincoln

We find evidence for a surface to bulk core level shift in both the Co 2p and Fe 2p core level photoemission spectra of 5.5 nm $CoFe_2O_4$ (111) film grown on Al_2O_3 (0001). The Co $2p_{3/2}$ and Fe $2p_{3/2}$ surface components were distinguished from the bulk components by angle resolved X-ray photoemission spectroscopy (ARXPS). While many complex oxides show a strong preferential surface termination, the surface termination of $CoFe_2O_4$ (111) contains both Co and Fe, but the core level photoemission binding energy shifts tend to indicate that the surface is significantly different from the bulk, even for so thin a film. Furthermore, X-ray photoemission spectroscopy (XPS) measurement of 1.7 nm $CoFe_2O_4$ (111) film grown on Al_2O_3 (0001) shows a suboxide interlayer of cobalt. We compare the surface properties of $CoFe_2O_4$ thin films with that of $NiFe_2O_4$ thin films. This has implications for cobalt ferrite as a magnetic storage media and could affect growth of this spinel in the degradation of steel in boiling water nuclear power applications.

SS-Contributed On Demand-100 Chemistry of Titanium Deposition Precursors for Area-Selective Deposition on Functionalized Silicon*, Tyler Parke,* *D. Silva-Quinones,* University of Delaware*; G. Wang,* Sandia National Laboratories, USA*; A. Teplyakov,* University of Delaware

Atomically precise and area-selective deposition processes are vital to the miniaturization of devices in modern electronics. Here, the selectivity of the titanium atomic layer deposition (ALD) precursors, $TiCl_4$ and TDMAT (tetrakis(dimethylamido)titanium), on hydroxyl, hydrogen, and chlorine-terminated Si(111) and Si(100) surfaces was investigated. Ex situ X-ray photoelectron spectroscopy (XPS) demonstrated that $TiCl_4$ readily deposits on HO-Si and to a lesser degree, on H-Si, but is relatively inert to Cl-Si. Atomic force microscopy (AFM) showed growth of smooth films on HO-Si, but delayed nucleation onto hydroxyl- containing defects in the H-Si surface. Density functional theory (DFT) simulations suggested the favorable chemisorption of $TiCl_4$ onto hydroxyl-containing surfaces in HO-Si and defected H-Si models. Thermal atomic layer deposition of TiO_2 with $TiCl_4$ and water on these surfaces was also compared with a commercial ALD process utilizing TDMAT and water.

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SS-Contributed On Demand-103 GRISU – Bonds in Focus

David Rath, *J. Pavelec, G. Parkinson, M. Schmid, U. Diebold,* TU Wien, Austria

The IRAS system GRISU (**GR**azing incident **I**nfrared absorption **S**pectroscopy **U**nit) was developed for investigations of adsorbates on oxide single crystals with maximum sensitivity. GRISU combines the commercially available FTIR spectrometer Bruker Vertex 80v with an UHV chamber [1]. All the optical components are mounted precisely in respect to each other to ensure the high performance requirement also after long term use, and the compact design requires just one CF150 flange (8" O.D.) on the UHV chamber.

The system features five mirrors for beam guidance placed in HV and UHV environment, and optimises the system's performance, flexibility and usability. Two of these mirrors are mounted on motorised kinematic mounts. One aperture allows to 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 result is a small controllable focal-spot diameter (max. 3 mm) on the sample.

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 on the sample. Compared to a commercially available system with two parabolic mirrors with a focal length of 250 mm, this is higher by a factor of about 20.

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SS-Contributed On Demand-106 RRKM Treatment of HCl Dissociative Chemisorption on Au(111): Reactive Dampening through Inefficient Translational Coupling and an Active Surface

Mark Bernard, *I. Harrison,* University of Virginia

Microcanonical unimolecular rate theory is applied to Shirhatti *et al.'s* recent supersonic molecular beam experiments examining the activated dissociative chemisorption of HCl on Au(111). A precursor mediated microcanonical trapping (PMMT) model [where the surface vibrates and HCl rotations, vibration, and translation directed along the surface normal are treated as active degrees of freedom] gave dissociative sticking coefficient predictions that are several orders of magnitude higher than experimental values, but in good accord with prior quantum and molecular dynamics simulations. Density functional theory electronic structure calculations using the PBE functional served to fix the vibrational frequencies of the reactive transition state and the threshold energy for dissociation, E_0 = 72.9 kJ/mol. To explore the possibilities of varying threshold energy, coupling to phonons, and dynamics, a three-parameter [E_0, s, ε_n] dynamically-biased (d–) PMMT model was fit to the experiments. A dynamical bias was introduced using an efficiency, ε_n, of normal translational energy to contribute to the active exchangeable energy capable of promoting reactivity. To achieve the low sticking probabilities observed in experiment, severe normal translational energy dampening ($\varepsilon_n \rightarrow 0.38$) was imposed, leading to a large vibrational efficacy of $h_v=e_v/e_n=2.6$. Despite this high vibrational efficacy, the experiments were relatively insensitive to vibrational energy at all but the lowest normal translational energies.The optimal threshold energy for dissociation was E_0 =31.8 kJ/mol, some 41 kJ/mol below the PBE-DFT prediction. Increasing the number of Au surface oscillators, s, capable of exchanging energy with HCl in the transient collisionally formed precursor complexes, correlated to a decrease in dissociative sticking at all translational energies, designating lattice vibrations as a dissipative channel. The d-PMMT modeling indicates that the HCl/Au(111) reactivity may be consistent with electronically adiabatic passage across a relatively low and late transition state that dynamically disfavors normal translational energy and admits energy dissipation to phonons.

SS-Contributed On Demand-109 Fast Diffusive Behavior of Pb on Ge(111) at Low Temperatures During Island Formation

Andrew Kim, *E. Baum, S. Chiang,* University of California at Davis*; M. Tringides,* Ames Laboratory, Iowa State University*; V. Stroup, D. Le, A. Childs, T. Rahman,* University of Central Florida

Lead deposited on Ge(111) at low temperatures (200-273K) was found to show unusual collective diffusion behavior after achieving a critical coverage (about 1.5ML). Depending on the temperature of the sample at the time of deposition, the size and number density of the Pb nucleated islands vary. From LEEM real time images, a high rate of movement of Pb atoms was found at the beginning of island formation, which was too fast to be explained by thermal diffusion. In order to measure the diffusion barrier of this unusual process, experiments were performed to follow the growth of these islands, with additional deposition beyond the critical coverage at constant temperature. Similar behavior was seen with Pb on Si(111) at low temperatures,[1] with island formation whose heights were determined by quantum size effects,[2] as well as unusually fast diffusion speed.[3] In order to explain the diffusing behavior of Pb, we also present a first-principles study of the structure of Pb overlayers on Ge(111) using DFT calculations, which were inspired by experimental observations of Pb/Ge(111) phases.[4]

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SS-Contributed On Demand-112 Selective Catalytic Chemistry at Rhodium (II) Nodes in Bimetallic Metal–Organic Frameworks

Deependra Shakya, *D. Chen, O. Ejegbavwo, N. Shustova,* University of South Carolina*; K. Vogiatzis,* University of Tennessee Knoxville*; A. Frenkel,* Stony Brook University/Brookhaven National Laboratory*; S. Senanayake,* Brookhaven National Laboratory*; A. Brandt,* University of South Carolina*; A. Ebrahim,* Stony Brook University/Brookhaven National Laboratory

Gas-phase catalytic activity has been studied at the metal nodes of metal-organic frameworks (MOFs), which provide the ability to control the geometry and ensemble size of active metal sites. We report one of the first studies of a gas-phase reaction catalyzed by isolated, highly dispersed sites at the metal nodes of a crystalline metal-organic framework (MOF). $(Cu_xRh_{1-x})_3(BTC)_2$ (abbreviated CuRhBTC, where BTC^{3-} =benzenetricarboxylate) is prepared from Rh^{3+} and CuBTC (HKUST-1) by post-synthetic ion-exchange. X-ray photoelectron spectroscopy and X-ray absorption near edge structure (XANES) were used to identify the oxidation state of Rh in CuRhBTC as +2. These Rh^{2+} sites are active for the catalytic hydrogenation of propylene to propane at room temperature, and the MOF structure stabilizes the Rh^{2+} oxidation state under reaction conditions. Scanning transmission electron microscopy experiments indicate that the Rh ions are uniformly dispersed on the nanoscale, and Raman spectroscopy studies demonstrate that bimetallic Cu-Rh nodes are formed. Density functional theory calculations suggest a mechanism in which H_2 dissociation and propylene adsorption occur at the Rh^{2+} sites.

SS-Contributed On Demand-115 Electron Stimulated Desorption from Ethane Condensed on Rare Gas Surfaces

Sramana Kundu, *M. Schaible, T. Orlando,* Georgia Institute of Technology, USA

The process of desorption induced by electronic transitions (DIET) is important in surface chemistry and physics. It is relevant in almost every system where solid surfaces are impacted by energetic particles, like surface modification processes in the laboratory to cold dust grains exposed to ionizing radiation in the interstellar medium. Study of such processes can help us understand chemical bonding on surfaces, charge and energy transfer, conversion of electronic energy to kinetic energy of the adsorbate, etc. Analysing the cations generated by electron stimulated desorption (ESD) from the adsorbed molecule is one way to do that. In general, fragmentation and ion desorption from species adsorbed on metals are quenched due to interactions with the metal substrate. Depositing the molecules on multilayers of rare gases overcomes this problem by localizing the electronic excitation on the adsorbate. The use of different rare gases – argon, krypton and xenon – leads to differences in the fragmentation and desorption processes of the same adsorbate, revealing how energy exchange occurs in each case.

Sub-monolayer quantities of ethane (C_2H_6), the simplest hydrocarbon with C–C and C–H bonds, was deposited on about 50 monolayer (ML) thick rare gas adsorbed on Ag substrate held at ~14 K in an ultra-high vacuum (UHV) chamber (base pressure = 5 x 10^{-10} torr). The sample was irradiated with electrons of specific energy using a pulsed electron gun. The positive ions are collected and analysed with a time-of-flight mass spectrometer (TOFMS) with a multichannel plate (MCP) detector. Mass spectra is collected at several energies between 15 and 50 eV and compared.

The threshold electron energy for ions generated from ethane is 15 eV for Ar and Kr, and 17 eV for Xe. The ion intensities from the rare gases follow the order Ar > Kr > Xe for the entire range we studied. The most likely mechanism is the ionization of the rare gas followed by charge transfer from the rare gas to ethane, causing its ionization and fragmentation. The ionization energy gap between the rare gases and ethane is in the order Ar > Kr > Xe, which is reflected in the ion intensities from the respective rare gas. The branching ratios of the observed ions - CH_3^+, $C_2H_2^+$, $C_2H_3^+$, $C_2H_4^+$, $C_2H_5^+$ and $C_2H_6^+$ - are calculated at each energy. $C_2H_4^+$ is the most intense fragment in the mass spectra in the threshold region (15-20 eV) for all three rare gases. The ratios change with energy and with the identity of the rare gas. This is because the energy available for the formation and subsequent desorption of a given fragment ion depends on the energy transfer process with the rare gas on which the molecule resides.

**SS-Contributed On Demand-118 Investigation of the Initial Stages of Iron Surface Oxidation and Corrosion at the Liquid/Solid and Gas/Solid Interface Using *in situ* Surface Spectroscopy*, Chathura de Alwis*, *M. Trought,* Michigan Technological University*; S. Nemsak,* Advanced Light Source, Lawrence Berkeley National Laboratory*; K. Perrine,* Michigan Technological University

Redox reactions of iron and their oxides maintain the balance of water, mineral and plant nutrient cycles on earth. Iron corrosion is a spontaneous electrochemical process, where iron serves as the anode and water and O_2 drive the cathode reaction. Ions, such as chlorides, are known to catalyze the surface reduction-oxidation reaction of iron and initiate the corrosion by breakdown of the native oxide layer. The rate of corrosion and the chemical composition of mineral scale formed at the metal surface depends upon the chemical environment of the electrolyte. Alkali chlorides catalyze surface oxidation of iron leading to the corrosion and metal degradation forming complex oxide films as the major products of corrosion.

To address these complex reactions, we developed a method utilizing polarized modulated infrared reflection absorbance spectroscopy (PM-IRRAS) and the meniscus method with our custom-build liquid cell to investigate the real-time redox processes at air/electrolyte/iron interfaces. This technique allows for probing the air/liquid/solid interface simultaneously of spontaneous redox reactions as a function of time under ambient conditions. In this study, a NaCl(aq) electrolyte was used as a model system as part of the air/electrolyte/iron interface. The interfacial oxidation of iron and mineral formation was strongly affected by the chemical properties of electrolyte. A considerable difference was observed at the interface, where the chemical composition of the minerals grown from gradual exposure to atmospheric O_2 and CO_2 compared to the fully submerged region of iron in NaCl(aq) with limited exposure to air (O_2 and CO_2). These results were supported with *ex situ* ATR-FTIR and XPS analysis.

These studies were compared to the initial stages of iron oxidation using ambient pressure (AP)-XPS at the gas/solid interface. A droplet of NaCl(aq) was exposed to the iron surface and then oxidized with various pressures of water and O_2 up to 100 mTorr. It was found that surface carbonate was produced, primarily from the combined oxidation of surface hydrocarbons, and a corresponding change in the anion/cation ratio. These studies of the initial stages of iron surface oxidation at the air/liquid/solid interface and the gas/solid interface advance our understanding of how ions from NaCl(aq), O_2 and H_2O affect the corrosion mechanism. This research suggest that ions play a critical role in the various stages of corrosion and the resulting mineral formation that impact environmental processes.

SS-Contributed On Demand-121 STM Studies of Alkanethiolate Reactivity with Atomic H as a Function of Temperature & Chain Length*, Sarah Brown*, *J. Sayler, S. Sibener,* University of Chicago

Thiolate self-assembled monolayers (SAMs) provide platforms for easily customizable organic interfaces, making them an excellent model system for studying the chemical properties of organic thin films. In particular, their reactions with atomic gas species yield important information about gas-surface interactions in organic films, specifically how static and dynamic disorder influence passivation. We have investigated the reactions of these SAMs with atomic hydrogen (H), using an angle-directed atomic gas source and *in situ* ultra-high vacuum scanning tunnelling microscopy (UHV-STM). First, a series of alkanethiolate samples of varying chain length (8- to 11-carbon atoms long) were reacted with H, resulting in the monolayers' conversion from close-packed standing-up phase to lower density lying-down phase. It was found that small increases in chain length caused disproportionately large decreases in reactivity at room temperature. This reaction progression was described using an exponential model containing two rate constants: a slow rate for hydrogen reactivity with standing-up phase, which is dependent on chain length, and a fast rate for low-density phase reactions, which is the same for all samples. Chain length-dependent changes in surface morphology were also observed, with short chain SAMs experiencing significant vacancy island reconstruction throughout the reaction compared to longer chain SAMs. Finally, the effect of temperature on the reactivity of decanethiolate SAMs was studied by reacting them with H at lower temperatures (130 K, 250 K and 270 K). The SAMs' reactivity was greatly reduced at lower temperature, with longer reaction times for 270 K and 250 K, and no visible reaction occurring at 130 K. Furthermore, there was a noticeable change in the reaction mechanism at 250 K, indicated by the fact that the originally-proposed two-rate constant model could not describe the 250 K experimental data. The changes in surface morphology during the reaction also differed significantly at 250 K. Reduced thiol mobility, lower surface energy, and increased lateral forces between chains at lower temperature are proposed to contribute to these changes in reactivity.

SS-Contributed On Demand-124 Surface Chemistry of 2-Propanol on SnO_2(101) Studied Using Ambient-Pressure X-Ray Photoelectron Spectroscopy*, Jessica Jenkins*, *R. Elzein, R. Addou, G. Herman,* Oregon State University

Tin dioxide (SnO_2) surface terminations can strongly impact surface reducibility especially under vacuum at different temperatures. For SnO_2 surfaces, tin ions can be in either the Sn^{4+} or Sn^{2+} oxidation state and this provides flexibility in controlling defect chemistries and catalytic properties. For example, studies have shown that the Sn^{+4}/Sn^{+2} ratio can significantly impact the activity of CO oxidation on SnO_2 nanomaterials. SnO_2(110) and SnO_2(101) surfaces have significantly different surface structures and temperatures where the surfaces become reduced in vacuum. Prior studies using low energy ion scattering indicated that the SnO_2(110) and SnO_2(101) initially had changes in their surface composition at ~440 and ~550 K, respectively. Recently we have shown that the reaction of 2-propanol on SnO_2(110) follows a Mars–van Krevelen reaction mechanism, where surface oxygen vacancies are formed during the surface reaction with 2-propanol. For this study, we have used ambient pressure X-ray photoelectron spectroscopy (AP-XPS) and low energy electron diffraction (LEED) to characterize the SnO_2(101) surfaces and used AP-XPS and *in situ* mass spectrometry to characterize the oxidation reactions. Experiments were performed on the SnO_2(101) surface for 2-propanol pressures up to 1 mbar, various 2-propanol/O_2 ratios, and a range of temperatures. During this presentation we will compare our experimental results to those we have previously obtained from the SnO_2(110) surface and relate these to the observed chemistries and the differences in surface structure.

SS-Contributed On Demand-127 Bi-Induced Shape Change of Homoepitaxial InAs(110) Surface Structure*, Brandon Carter*, *J. Millunchick,* University of Michigan

Bi surfactants have a profound effect on the surface morphology of III-V semiconductors [1]. They induce a large anisotropy in adatom diffusivity on (001) GaAs surface, which can either smoothen films or cause mounding along the [1-10] [2]. Bi surfactants are also used to drive the self-assembly of (110) InAs quantum dots on GaAs(110) by changing the growth mode from 2D to 3D [3]. This work examines the Bi-induced change in surface morphology on homoepitaxial InAs(110), by growing 20 period InAs:Bi superlattices at T=290°C. Each period consisted of 30nm of InAs followed by exposure to Bi flux for times 0<t<45s. The top surfaces of the films were characterized using tapping mode atomic force microscopy. During homoepitaxial growth, large faceted trapezoidal mesas ~4 µm in diameter and 340 nm tall form on the surface with flat regions in between. The parallel edges of the trapezoid are aligned perpendicular to the [001], while the side legs are aligned along the [1-1-3]and [-11-3]. The morphology between the mesas is defined by a scalloped, or semicircular, step structure that is relatively flat, with root mean squared (RMS) roughness of 14 nm. At a Bi exposure of t=15s, the mesas shrink both in diameter and height and the background roughens such that RMS=55nm. But as more Bi is deposited, the surface smooths such that at t=45s RMS=24nm. The mesas also undergo a Bi-induced shape change; specifically, the alignment of the trapezoidal legs start to shift towards lower indices beginning at t=15s and becoming more prominent as more Bi is deposited, such that the legs align along the [1-1-1] and [-11-1] at t=45s. Closer analysis reveals that the changes in surface roughness and island shape are related to a change in step structure. Without Bi the steps perpendicular to the [001] are straight and are comprised of bunches ~19 nm tall. However, the steps unbunch as Bi is deposited with step bunching height ~3nm tall at t=45s. The steps also begin to meander with the addition of Bi. Bi does not form droplets on these surfaces, in contrast to reports of growths on the (001) InAs surface [4], thus leading to higher Bi incorporation on the (110) compared to the (001) . These observations together show that the energetics of the (110) are vastly altered by Bi and may suggest an atomic mechanism for surface segregation.

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SS-Contributed On Demand-130 Patterned and Graded ALD Coatings for Imaging and Spectroscopy Applications*, **April Jewell**, J. Hennessy, S. Nikzad,* Jet Propulsion Laboratory

We present an overview of our work using atomic layer deposition (ALD) to develop optical coatings for silicon detectors. To date, our team has taken advantage of the spatial uniformity of ALD for device passivation, antireflection coatings, and optical filters. Our current work is aimed at introducing spatially varying detector response spanning the ultraviolet (UV) and visible wavelength ranges. Intentionally introduced spatial non-uniformities (i.e. patterning) in a coating, for example, would allow one to match a detector's spatial response relative to the incident wavelength for spectrograph applications.

Two approaches will be discussed, including Area Selective (AS) and Spatial (S) ALD. We report on an AS-ALD investigation on the patterning of aluminum fluoride (AlF_3) antireflection coatings. We explored AlF_3 deposition directly on bare silicon and on silicon pre-coated with lithium fluoride (LiF). We examined the effect of different aluminum precursors, including trimethylalumnium (TMA), triethylaluminum (TEA), dimethylaluminum hydride (DMAH), and hexakis (dimethylamino) dialuminum (TDMAA); in all cases the F precursor was hydrofluoric acid (HF). We show that the TMA/HF ALD reaction was completely inhibited when attempting to deposit AlF_3 films directly on LiF; while the other precursors showed varying levels of inhibition. We also use SALD to develop coatings with a graded thickness across a detector surface, which could potentially result in more subtly varying transitions in detector response from one end to the other.

When combined with JPL's delta-doped silicon detector technology, the development will result in detectors with high quantum efficiency (QE) in targeted wavelength bands, allowing for more versatile UV–Visible instrumentation including spectrometers. The advancement will enable more affordable, and less complex, high-performance instruments and thus addresses NASA's strategic objectives.

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SS-Contributed On Demand-133 Beyond the Ligand Exchange Model – Time Resolved ALD of HfO2 on InAs Thermal Oxide*, **Giulio D'Acunto**, P. Shayesteh, F. Rehman,* Lund University, Synchrotron Radiation Research, Sweden*; E. Kokkonen,* MAX IV Laboratory, Lund University, Sweden*; R. Timm, J. Schnadt,* Lund University, Synchrotron Radiation Research, Sweden

Atomic layer deposition (ALD) is a powerful technique for the highly controlled deposition of thin-film materials. Its parent techniques, chemical and physical vapor deposition, have been popular for a long time. In contrast, ALD – invented in the 1960s & 1970s – has become increasingly important only since the turn of the new century. This is illustrated by the fact that 18,000 studies on ALD have been published during the past two decades. In the past five years even an average of 1,500 publication per year has been recorded. Thus, nowadays ALD is central to a wide range of material technologies, including e.g. solar cells, transistors, and quantum materials.

The ideal ALD scheme is based on the self-limiting adsorption and reaction of two gaseous precursors with a substrate, in a sequential manner. The exposure of the substrate leads to the formation of not more than a monolayer. This is the origin of the excellent thickness control of ALD. However, despite its importance, particularly for the deposition of high-κ dielectrics, ALD still suffers from unknown surface reaction mechanisms and kinetics. The postulated ideal reaction path, based on a ligand exchanged model, and the passive role of the substrate needs to be revisited.

This study presents new insight into the ALD of HfO_2 on InAs(100) from TDMAHf and water obtained by in situ ambient pressure XPS (APXPS). InAs is an optimal material for the generation of future high-speed MOS due to its higher electron mobility and smaller band gap as compared to silicon. However, the high defect density at the interface between the semiconductor and its native oxide surface has impacted the usability of InAs in MOSFET devices. The ALD of Al_2O_3 and HfO_2 on III-V semiconductors, however, helps to improve the performance of InAs significantly due to the self-cleaning effect that occurs during the early stage of ALD. From APXPS we found that the unwanted oxide despite its thickness is entirely substituted by the desired high-κ oxide already in the first ALD half-cycle, where the high-κ oxide layer is limited to one monolayer. The reaction stops once all oxygen is consumed. The interface between the InAs bulk and the Hf oxide is composed of In-O-Hf. The formation reaction proceeds in the absence of surface hydroxyls, i.e. not according to the hydroxyl-based standard ligand exchange model. Instead, a bimolecular β-hydride elimination reaction is found to lead to the formation of methyl methylene imine. Furthermore, we will present detailed dynamics of the initial surface reactions which cannot be correctly described by the standard ALD model. Time-resolved ambient pressure XPS closes an important gap through its ability to monitor the ALD chemistry while it is ongoing.

SS-Contributed On Demand-136 The Roles of Subsurface Hydrogen and Adsorption of Water on Ni(111)*, **Maxwell Gillum**, M. Turano, E. Jamka, D. Killelea,* Loyola University Chicago

Gas-phase H atoms readily absorb into interstitial sites on Ni(111) at temperatures below 140 K, leaving a H-saturated surface.The surface adsorbed H may be removed using collision-induced recombinative desorption.I will present preliminary results demonstrating the ability to prepare clean Ni(111) surfaces loaded with subsurface D atoms.We will use these surfaces to investigate isotope exchange between adsorbed water and the subsurface D(H) atoms.I will also study how the presence of small amounts of adsorbed oxygen atoms on the Ni surface influence isotope exchange.These results will shed light on how subsurface species can influence surface-mediated reactions.

SS-Contributed On Demand-139 Oxidation of Sn at the Cluster-Support Interface: Sn and Pt-Sn Clusters on TiO_2(110)*, **Sumit Beniwal**,* University of South Carolina*; W. Chai,* University of Texas at Austin*; K. Metavaryuth, T. Maddumapatabandi, D. Shakya,* University of South Carolina*; G. Henkelman,* University of Texas at Austin*; D. Chen,* University of South Carolina

The growth of Sn and Pt-Sn clusters on TiO_2(110) has been studied by scanning tunneling microscopy (STM), X-ray photoelectron spectroscopy (XPS), low energy ion scattering (LEIS) and density functional theory (DFT).At low Sn coverages (0.02 ML), single-layer high clusters of SnO_x are formed with a narrow size distribution and uniform spatial distribution.XPS experiments indicate that these clusters consist of oxidized Sn, and a corresponding reduction of the TiO_2 substrate is observed.At higher Sn coverages, the surface is still dominated by two-dimensional clusters of SnO_x, but larger three-dimensional clusters of metallic Sn also appear.As the Sn coverage is increased, the number of three-dimensional clusters increases, and the ratio of Sn:SnO_x increases, suggesting that SnO_x and reduced TiO_x form at the cluster-support interface. When Pt is deposited on top of the Sn/SnO_x clusters, the relatively mobile Pt atoms diffuse on the surface and become incorporated into existing Sn/SnO_x clusters.Furthermore, the addition of Pt to the Sn/SnO_x clusters causes the reduction of SnO_x to metallic Sn and the oxidation of Ti^{3+} to Ti^{4+}; this behavior is attributed to the formation of Pt-Sn alloy clusters, which results in the diffusion of Sn away from the interface with the TiO_2 support.In contrast, when Sn is deposited on an equal coverage of Pt clusters, new Sn/SnO_x clusters are formed that coexist with Pt-Sn clusters.However, the surfaces of both Pt on Sn and Sn on Pt clusters are Sn-rich due to the lower surface free energy of Sn compared to Pt.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.

SS-Contributed On Demand-142 Excited State Relaxation Dynamics in HOPG Using Pump-Probe Momentum Microscopy in the Perturbative Limit*, Sergii Chernov*, *J. Bakalis, A. Kunin, C. Corder, P. Zhao,* Stony Brook University*; M. White,* Brookhaven National Laboratory*; G. Schönhense,* Johannes Gutenberg-Universität Mainz, Germany*; T. Allison,* Stony Brook University

Angle-resolved photoemission spectroscopy (ARPES) has proven to be one of the most powerful techniques for ground state electronic structure studies. Abilities to directly visualize the electron E-vs-$k_{\parallel}$ distributions, access to the spin degree of freedom[1] and other photoemission effects[2] often make ARPES the method of choice for material electronic properties and crystal structure investigations. Modern ultrafast lasers utilizing high-order harmonic generation (HHG) further enable time-resolved ARPES (TR-ARPES) capable of probing short-lived excited electronic states and their dynamics via pump-probe experiments. However, most HHG-based ARPES systems suffer from relatively low pulse repetition rates. This severely limits the range of experiments that can be conducted and the parameter space that can be explored in TR-ARPES experiments in complex materials.

In order to overcome the aforementioned problems,we combine two state-of-the-art approaches: a high repetition rate HHGXUV generation[3]and Time-of-Flightmomentum microscopy[4]. The XUVsource operating at 61.3 MHz enables experiments at low pump fluences and substantially mitigates the space charge problem. The momentum microscope at the given ~16 ns periodallows to collect simultaneously electron distributionswithin the full Brillouin zone (BZ)andenergy intervalsof up to 3 eV with ~50 meV resolution. Finally, the tight XUV beam focus of less than 30 µm FWHM and further sample region selection with the field aperture of the momentum microscope apertures allow for pump-probe micro-ARPES experiments in perturbative limit with pump pulse energiesdown to nJ/cm^{2}scales.

We will presentan example study on graphiteusing 515 nm (2.41 eV) *p*-and *s*-polarized pump light. Measurements were performed with different probe energies, i.e. different $k_{\perp}$ cuts of the BZ across H and K points. A range of pump fluences from 1 to 100 µJ/cm^{2}wereexplored to ensure non-perturbative excitation character.The full BZ data accumulated allows the extraction of fundamental electron-phonon and electron-electron scattering processes with unprecedented detail.

SS-Contributed On Demand-145 C-H Bond Dissociation of Methane on Rh(111): Remarkable Activity of Step Sites*, Xingyu Wang*, *I. Harrison,* University of Virginia

Steam reforming is one of the most important industrial chemical processes. However, it is usually performed in large-scale reactors and has high energy demand. Catalytic partial oxidation of methane, on the other hand, can be carried out in compact and low capital-cost reactors to produce syngas. Rh is generally considered the best metal catalyst for partial oxidation.

We studied the initial C-H bond cleavage of methane under non-equilibrium conditions on Rh(111), where the temperature of the impinging gas molecules could be different from the surface temperature, and the angle of incidence of the impinging molecules could be varied. This was realized in an ultra-high vacuum chamber with a heated effusive molecular beam doser, which generates a beam of molecules with a cosine angular distribution and energy distributions fully thermalized to the doser temperature. The surface temperature of the Rh(111) crystal could be controlled independently and carbon deposited on the surface was measured by Auger electron spectroscopy, which allowed dissociative sticking coefficients to be determined.

Using a precursor mediated microcanonical trapping model, molecular translational energy directed along the surface normal was found to be about twice as effective as vibrational energy in promoting the reactivity of methane. Unlike on the Pt (111) surface where (111) terrace site reactivity dominates, methane reactivity on Rh (111) indicates that Rh step sites are not easily poisoned by C accumulation and can contribute substantially to the overall methane reactivity, especially at lower temperatures. Such multidimensional reactivity studies allow for relatively facile designation of the terrace and step activity which allows us to reconcile single crystal and Rh foil reactivity studies.

Surface Science Division

Room On Demand - Session SS-Invited On Demand

Surface Science Invited On Demand Session

SS-Invited On Demand-1 Halide Ion Mobility in Metal Halide Perovskites and its Impact on Photovoltaic Performance*, Prashant Kamat,* University of Notre Dame **INVITED**

The intrinsic ionic defects, specifically halide ion vacancies, often dictate the mobility of halide species within the perovskite film during the operation of solar cells.Of particular interest is the halide ion mobility in metal halide perovskites, which plays an important role in determining the performance of perovskite solar cells. Photoinduced phase segregation seen in mixed halide perovskite films under steady state irradiation offers a convenient way to visualize halide ion segregation. Interestingly, upon storage in dark, the process is reversed and the original mixed halide composition gets restored. Whereas entropy of mixing explains the thermally activated mixing of halide ions to yield mixed halide perovskite, the opposite trend observed during photoirradiation remains an intriguing phenomenon.The threshold energy of incident light to observe halide segregation increases with increasing temperature. The diffusion of these halide species, which is tracked through changes in the absorption spectra at different temperatures, offers a direct measurement of thermally activated halide diffusion in perovskite films. The thermally activated halide exchange shows the challenges of employing layers of different metal halide perovskites in stable tandem solar cells.

SS-Invited On Demand-7 Chemistry and Hydrogen Bonding Environment at Environmental Surfaces as Seen by X-ray Photoelectron and Electron Yield NEXAFS Spectroscopies*, Markus Ammann,* Paul Scherrer Institut, Switzerland **INVITED**

X-ray photoelectron spectroscopy (XPS) of typically core atomic electronic levels provides chemical composition information and electron yield near edge X-ray absorption fine structure (NEXAFS) spectroscopy gives insight into the structure of the local molecular environment. The low inelastic mean free path of electrons of a few nanometer enables sensitivity for the condensed matter – gas interfacial region. The development of ambient pressure electron analyzers has offered tremendous opportunities for molecular understanding of environmentally relevant aqueous solution surfaces, ice surfaces, and mineral oxides, all in presence or absence of reactive trace gases and in or out of equilibrium with water vapor. Applications involving the characterization of interfacial structure at mineral oxides and ice, the protonation state of acids or the direct observation of reaction intermediates at the surface of liquid water will be presented.

SS-Invited On Demand-13 Thin Film Growth One Step at a Time: Unraveling Mechanisms in Atomic Layer Deposition*, Stacey Bent,* Stanford University **INVITED**

With the growing interest in functional nanoscale materials for applications such as electronics, catalysts, and batteries, methods for fabricating materials with atomic-level control are becoming increasingly important. Atomic layer deposition (ALD) is a vapor-based method that provides excellent capabilities for depositing thin solid films, nanoparticles, and other nanoscale materials. Based on sequential, self-limiting vapor-surface reactions, ALD offers exceptional conformality, thickness control at the Angstrom level, and tunable film composition. This talk will describe research into the fundamental processes that drive ALD. Two ALD systems will be presented in which a combination of characterization methods is applied to elucidate nucleation and growth mechanisms. In the first system, ALD of binary and ternary metal oxides using ozone as a counterreactant show unusual behavior implicating the importance of trapped reactive oxygen species in these ALD processes. For example, in the growth of ternary Ni-Al-O films using supercycles of nickel oxide and aluminum oxide ALD, Al uptake is greatly enhanced when Al_2O_3 ALD followed a NiO ALD cycle, a result that may arise from the presence of nickel superoxide species after ozone exposure. In ALD of iron oxide by t-butylferrocene and ozone, growth per cycle of greater than one monolayer of Fe_2O_3 per cycle is observed and explained by the presence of excess oxygen stored in the surface regions of deposited films. In the second system, ALD of MoS_2 thin films as well as ALD of metal oxides on MoS_2 will be described. We show that the concentration and size of ZnO nanocrystals grown on MoS_2 by ALD can be independently tuned by controlling the growth conditions. We also introduce a kinetically-driven ALD process for growing stoichiometrically controlled, crystalline MoS_2 from $Mo(CO)_6$ and H_2S at temperatures as low as 190 °C. Insights into the effect of ALD process conditions on growth behavior and materials properties will be presented.

SS-Invited On Demand-19 Interaction of Small Heteroatomic Organic Compounds with Ceria*, Ye Xu,* Louisiana State University **INVITED**

Ceria is an abundant and versatile technological material owing to its ability to readily change between oxidation states and store, release, and conduct oxygen.Its surfaces present regular arrays of acidic, electrophilic Ce cations ($Ce^{\delta+}$) and basic, nucleophilic O anions ($O^{\delta-}$) in close proximity, accessible to different extents depending on the crystalline facet and degree of surface reduction.Because of the amphoteric nature of its surfaces, ceria can interact strongly with a variety of Brønsted/Lewis acid/base compounds, oxo compounds (molecules derived from oxoacids such as aldehydes, ketones, esters and phosphates), and their heteroatomic counterparts.I will present the findings of our theoretical investigation into the adsorption of several such organic compounds and their reactivity on ceria in terms of energetic, geometric, electronic, and vibrational properties.Reactivity patterns that make this oxide potentially useful for catalyzing a broad range of organic reactions under mild conditions will be discussed.

Thin Films Division
Room On Demand - Session TF-Contributed On Demand
Thin Film Contributed On Demand Session

TF-Contributed On Demand-1 Improved Impedance Spectroscopy Model of Interfaces for CZTSe Ge Bi-Layers Solar Cells*, Sanghyun Lee,* Indiana State University*; K. Price,* Morehead State University*; E. Saucedo,* Catalonia Institute for Energy Research, Spain

Impedance spectroscopy is an advanced technique that could provide an opportunity to model the physical parameters of a system of interest with an equivalent circuit (EC). From our preliminary work, we developed thin-film CZTSe solar cells with thin Ge bi-layers, which articulate the recombination mechanism of emerging CZTSe devices. We reported that the recombination of this weak CdS/CZTSe heterojunction interface is mitigated with the engagement of thin Ge nanolayer (<10 nm) at both interfaces by developing proper models. In particular, the response of quantum efficiency at the heterojunction interface with weak bias voltage and lights provided an accurate model to understand the complex nature of their interface.

In this contribution, we fabricated and characterized a set of CZTSe Ge nanolayer thin-film solar cells with DC magnetron sputtering by applying a refined advanced technique of impedance spectroscopy for AC response of the EC. The interfaces of CZTSe Ge bi-layers devices are modeled with the lumped bulk resistance in the system. The developed model is established with a constant phase element (CPE) for three critical interfaces, such as heterojunction, $MoSe_2$ interlayer, and metal back-contact. We used an in-house modeling tool in MATLAB environment, connected to external tools such as Sentaurus TCAD and LEVM/LEVMW. By incorporating nanoscale Ge bi-layers below and above the absorber, the improved back-contact barrier shows a good agreement of impedance spectroscopy with a proposed equivalent circuit model (chi-squared function = 4.19×10^{-4}). In particular, the introduction of a CPE minimized the deviation with the proposed EC model. The impedance of CPE is determined by the product of a dimensionless parameter, which value between zero and unity. As P of a CPE approaches to 1, the quality of interface and uniformity improves. A CPE indicates impedance with non-ideal frequency-dependent properties and a constant phase over the entire frequency. Collectively, the deviation from the ideal dependency is mainly due to a distribution in the current density coming from the material inhomogeneity. With the bulk resistance, 21.0 $\Omega \bullet cm^2$, P of interfaces between CdS/CZTSe, CZTSe/$MoSe_2$, $MoSe_2$/Mo are 0.957, 0.997, and 0.994, respectively. In particular, P of CZTSe/$MoSe_2$, $MoSe_2$/Mo interfaces approach to 1, which indicates the improved back-contact interface by adding 2.5 nm Ge near back contact interfaces. Resistances of two back-contact interfaces (12.4, 10.9 $\Omega \bullet cm^2$, respectively) are less than 0.3% of the CdS/CZTSe heterojunction interfaces. However, the heterojunction P showed the lowest value (0.957).

TF-Contributed On Demand-4 Atomic Layer Deposition for Enhanced Reactivity, Stability, and Sulfur Tolerance of Biomass Conversion Catalysts*, Wilson McNeary,* National Renewable Energy Laboratory*; K. Unocick,* Oak Ridge National Laboratory*; G. Lahti, S. Tacey, C. Farberow, M. Griffin,* National Renewable Energy Laboratory*; E. Wegener,* Argonne National Laboratory*; K. Van Allsburg,* National Renewable Energy Laboratory*; A. Dameron, K. Buechler,* Forge Nano*; D. Vardon,* National Renewable Energy Laboratory

Heterogeneous catalysts are an essential tool in the transition towards a sustainable, bio-based economy for fuels and chemicals. However, the harsh conditions (e.g., high temperatures, acidity, oxidizing/reducing environments) of many key biomass conversion processes give rise to nanoparticle sintering, support collapse, and metal leaching in conventional PGM catalysts. Active site poisoning due to the relatively high sulfur content of most biomass feedstocks further compounds these durability problems. Next-generation catalysts must be developed to address these stability challenges. In this work, we have used atomic layer deposition (ALD) to modify a conventional Pd/Al_2O_3 hydrogenation catalyst and generate improvements in its stability and sulfur tolerance, as well as overall catalyst activity. Ten cycles of TiO_2 ALD were applied to Pd/Al_2O_3 using a proprietary coating process developed by industry partners. The coated catalyst ($10cTiO_2$), alongside uncoated Pd/TiO_2 and Pd/Al_2O_3 controls, was characterized in-depth and naphthalene hydrogenation was used as a probe reaction to assess activity. The $10cTiO_2$ catalyst was observed to be significantly more active towards hydrogenation than uncoated Pd/Al_2O_3, despite evidence that the ALD coating suppressed chemisorption uptake through coverage of Pd. In order to reconcile these seemingly contradictory findings, interactions between the Pd nanoparticles and TiO_2 ALD coating were investigated via XAS and computational modeling. The catalysts were also assessed for their sulfur tolerance, thermal stability, and hydrothermal stability. Each of these catalyst stability parameters was enhanced by application of the TiO_2 ALD layer; the mechanisms by which the layer may have mitigated these degradation processes will be discussed. ALD technology holds great potential in the development of next-generation catalysts for biofuels and bioproducts and this work constitutes an important examination of the expected and unexpected benefits of applying TiO_2 ALD coatings to supported Pd hydrogenation catalysts.

TF-Contributed On Demand-7 Molecular Layer Deposition of All-Organic Polymer Films on Particles for Pharmaceutical Applications*, Tyler J Myers,* *S. George,* University of Colorado Boulder

Molecular layer deposition (MLD) utilizes sequential, self-limiting surface reactions to deposit polymeric thin films. Depending on the precursors, MLD polymeric films can be all-organic or a mixed organic-inorganic hybrid film. In this study, all-organic polyamide MLD films were deposited on particle substrates using adipoyl chloride (AC) and ethylene diamine (ED) as the reactants. This polyamide film is designated as Nylon 6,2. Very little work has been performed to use MLD to deposit all-organic polymer films on particles. This lack of studies may be attributed to the high surface area of particles and the low vapor pressure of the organic reactants. However, MLD of all-organic polymer films may be important for tuning the drug delivery of pharmaceuticals. All-organic polymer films are much more robust in aqueous solutions than organic-inorganic hybrid polymer films.

The polyamide MLD was performed in a rotating cylinder reactor to agitate the particles. The rotating cylinder reactor was located inside an isothermal enclosure to eliminate cold spots that cause difficulties when using low vapor pressure precursors. The polyamide MLD was performed at low temperatures ranging from 37°C to 80°C. These low temperatures allow the polyamide MLD film to be deposited on thermally sensitive organic particles, such as pharmaceutical particles. Using witness wafers in the reactor, the sequential AC and ED exposures led to a growth rate of 4 Å/cycle at 67°C as determined by x-ray reflectivity (XRR) measurements. This growth rate was in good agreement with the film thicknesses versus number of MLD cycles measured by transmission electron microscopy (TEM) on inorganic particles (ZrO_2) and organic particles (cellulose and active pharmaceutical ingredients).

The TEM images revealed that the polyamide MLD films were smooth and conformal on the particles.The MLD films could also be deposited with a linear growth rate on the various particle substrates. Fourier Transform Infrared (FTIR) vibrational analysis of the polyamide MLD films revealed the expected N-H, C-H, C-N, and C=O stretching vibrations and CO-N-H bending modes. X-ray photoelectron spectroscopy (XPS) analysis on witness wafers also yielded peaks corresponding to C, N, O, and a small amount of Cl. Energy Dispersive Spectroscopy (EDS) mapping of the polyamide MLD film grown on cellulose particles observed N and Cl in the polyamide coating. Dissolution testing of active pharmaceutical ingredients (APIs) showed an obvious extended release profile of the drug particles coated with an MLD film.These observations suggest that MLD of all-organic films on drug particles should be promising for tuning drug delivery.

TF-Contributed On Demand-10 40 Years of Kraut Valence Band Offset Measurements: The Good, The Bad, and The Ugly*, **Sean King,*** Intel Corporation*; M. Paquette,* University of Missouri - Kansas City

In 1980, E.A. Kraut in collaboration with R.W. Grant, J.R. Waldrop, and S.P. Kowalczyk published in Physical Review Letters (vol. 44, p. 1620) a core level referencing technique for the measurement of valence band offsets (VBOs) by X-ray photoelectron spectroscopy (XPS) that has been cited in thousands of semiconductor heterojunction band alignment studies. The popularity of the technique likely stems from the fact that it consists of three seemingly easy measurements: the relative position of the valence band maximum (VBM) to a deep core level in bulk material 1, the relative position of the VBM to a deep core level in bulk material 2, and the relative position of these same core levels from each material at their interface. Despite the apparent simplicity, such measurements are fraught with numerous complications that can in some cases lead to inaccuracies significantly more than the reported error bars (if even provided!) and widely different reported VBOs for nominally identical interfaces. Some of these effects are well known such as surface charging, core level peak fitting, and valence band maximum fitting. However, other effects and considerations such as differential charging, binding energy scale calibration, and the impact of surface cleaning (or not) are less well known. The cumulative result of the lack of consideration of these effects can result in sometimes questionable or highly speculative VBO measurements. In this article, we utilize a recent XPS study of a hafnium dioxide (HfO_2) interface with amorphous hydrogenated boron nitride (a-BN:H) to highlight some of the common and not so common issues that can appear when utilizing the Kraut method to determine the HfO_2/a-BN:H valence band offset. We present a checklist of important considerations and best known methods for performing Kraut XPS VBO measurements free of ambiguity and errors beyond the often quoted ± 0.1 eV accuracy. Our goal is to establish a dialogue and guidelines within the American Vacuum Society and greater scientific community for reviewing future articles utilizing the Kraut method to drive a more consistent approach and help minimize erroneous or questionable results from reaching JVST or related journals.

TF-Contributed On Demand-13 Covalently Crosslinked Organic Network Thin Films for Robust Surface Modification*, **Junjie Zhao,*** Zhejiang University, China

Robust surface modification provides long-term protection and maintains surface properties, which is desired in a wide variety of engineering applications. Covalently crosslinked organic networks typically exhibit better stability than linear polymers, but are difficult in processing into thin films by solution methods due to the insolubility in organic solvents. In comparison, initiated chemical vapor deposition (iCVD) avoids the use of solvents and directly forms crosslinked organic networks on substrate surfaces *via* free radical polymerization of adsorbed monomers. The control of the crosslinking degree together with simultaneous tuning of the surface energy represents a critical challenge for iCVD crosslinked polymers.

We developed an *in-situ* thermal annealing method for further enhancing the crosslinking degree of iCVD polymers after deposition. This process reduces the number of pendant vinyl groups present in the as-deposited polydivinylbenzene (PDVB) films, thus inhibiting the oxidation of iCVD PDVB in ambient conditions. Consequently, the low surface energy and hydrophobicity can be maintained for at least 2 months. Taking advantage of the excellent stability, we synthesized a few covalently crosslinked organic networks with low surface energy *via* iCVD for controlling the heterogeneous nucleation of $CaCO_3$ on the wall of heat exchangers in thermal desalination. We found that chemical stability is key to long-lasting modification and protection of Cu/Ni alloy. iCVD cyclosiloxane polymer films reduce the work of adhesion between $CaCO_3$ and Cu/Ni substrate by up to 5 times, while lowering the corrosion rate of Cu/Ni in boiling water by up to 190 times. By inhibiting the corrosion induced nucleation and increasing the energy barrier of $CaCO_3$ heterogeneous nucleation, iCVD poly(1,3,5-trivinyl-1,3,5-trimethylcyclotrisiloxane) (PV_3D_3) enables 14 times lower $CaCO_3$ fouling on Cu/Ni substrates at 110℃ in synthesized seawater.

TF-Contributed On Demand-16 Highly Conductive Nanograting-Nanohole Structures with Tunable and Dual-Band Spectral Transparency*, **Yanfeng Wang,*** Tsinghua University, China*; H. Chong, I. Choi,* University of Georgia*; Z. Zhang,* Tsinghua University, China*; Y. Zhao,* University of Georgia, China

Simultaneous increasing the electric conductance and optical transmission represents a key challenge for the development of the high-quality transparent metallic film. Using nanosphere lithography and oblique angle deposition, we show that large-area silver nanograting on nanohole structures (NGonNH) can meet this challenge with simultaneously improved electric property and optical transparency. The fabricated nanograting-nanohole hybrid structure exhibits an excellent sheet resistance as low as 4.53 Ω/□, an optical transmission of 75.4% from visible to near IR, and a high Haacke number up to 13.1, which is superior to previously reported metal nanohole networks or TMFs. The geometries of the formed NGonNH can be precisely varied by controlling the size of the polystyrene nanospheres (PSNS) monolayer, the etching duration of the PSNS, the orientation of the PSNS monolayer domain, and the vapor incident angle during deposition. Both the electric conductance and optical transparency are anisotropic and can be tuned by the nanohole diameter, lattice spacing, and the polarization of incident light. In particular, the transparency wavelength bands for different polarized lights are significantly different due to the plasmonic coupling effect as well as the anisotropic morphology of the nanograting-nanohole structure, which is very unique and has the potential application for polarization-modulation based optical components or sensors. The reduced and anisotropic electronic behavior is predicted by a two-dimensional hexagonal resistor network model, and the observed optical responses match well with the results from finite-difference time-domain calculations.

TF-Contributed On Demand-19 Rapid TiN Nucleation using Electron-Enhanced Atomic Layer Deposition (EE-ALD) with a Reactive Background Gas*, **Zachary Sobell,*** A. Cavanagh, S. George,* University of Colorado at Boulder

Ultrathin barriers in backend interconnects are needed to provide as much room as possible for conducting lines in vias.Rapid nucleation is required to achieve continuous ultrathin barrier films at a minimum thickness.To obtain rapid nucleation, we have employed electron-enhanced atomic layer deposition (EE-ALD) for the growth of TiN barrier films.We have also developed a new method of EE-ALD based on utilizing a reactive background gas concurrently with the EE-ALD process.The reactive background gas is possible when using a hollow cathode plasma electron source (HC-PES) because the HC-PES can operate with reactor pressures in the mTorr range.

For this work on TiN EE-ALD with a reactive background gas, tetrakis(dimethylamido) titanium (TDMAT) was used as the Ti precursor. The EE-ALD was performed using sequential TDMAT and electron exposures.During these sequential exposures, NH_3 was present continuously in the reactor as a background gas at ~1 mTorr.NH_3 is believed to be decomposed by the electron beam and liberate H and N radicals. The N radicals may facilitate the Ti nitridation. The H radicals may allow the removal of C as CH_4.Background gases were not possible during earlier EE-ALD work using an electron gun as the electron source because the hot filament of the electron gun would react with the background gas.

TiN film growth was observed to proceed rapidly during TiN EE-ALD using the NH_3 background gas.The TiN EE-ALD was performed at ~65 °C resulting from mild substrate heating by the incident electron beam. Linear TiN growth was observed beginning on the first EE-ALD cycle on the native oxide of a Si wafer.Longer nucleation times of ~7 EE-ALD cycles were monitored on in situ deposited Si_3N_4 films.On both substrates, the TiN EE-ALD growth rate was ~0.5 Å/cycle and the TiN film purity was high.In situ Auger electron spectroscopy (AES) routinely measured »91 at% Ti and N.The remaining AES signals were attributed to C and O.Ex situ XPS analysis also revealed a Ti:N ratio of ~3:4. This work demonstrates that reactive background gas can reduce possible contaminants during EE-ALD.The reactive background gas also opens up the possibility of utilizing many new precursor/background gas combinations for EE-ALD.

TF-Contributed On Demand-22 Structural and Chemical Evaluation of $Sc_xAl_{1-x}N$-GaN Heterostructures Grown by Molecular Beam Epitaxy*, **Joseph Casamento,*** H. Lee, C. S. Chang,* Cornell University*; M. F. Besser,* Ames Laboratory*; T. Maeda, D. A. Muller, H. Xing, D. Jena,* Cornell University

Scandium aluminum nitride (ScxAl1-xN) has gained tremendous interest in recent years due to enhanced piezoelectric and ferroelectric behavior from isoelectronic alloying with Sc. [1,2] Current challenges for next generation ScxAl1-xN-based optoelectronics include scaling down the active piezoelectric layers while still maintaining high structural quality and piezoelectric performance. MBE aims to solve this challenge and create ultrathin layers with sharp interfaces and high crystalline quality. GaN, a polar semiconductor with excellent optoelectronic properties is lattice matched to ScxAl1-xN at ~18% Sc and enables ultra-thin ScxAl1-xN to be highly piezoelectric.[3] Accordingly, GaN provides an excellent platform to study the fundamental properties of ScxAl1-xN by epitaxial stabilization and integration into commercial technology.

In this work, we report the first structural and chemical analysis of epitaxial ScxAl1-xN (x=0.1 to 0.45)-GaN multilayer heterostructures grown on metal polar GaN (0001) substrates using two different Sc metal sources. One Sc source was quoted as 99.99 % (4N) pure on a rare metals basis and another higher purity Sc source from Ames Laboratory was quoted as 99.9% (3N) total purity, including carbon and oxygen. Sc was supplied via electron beam evaporation and Al, Ga, and Si were supplied using Knudsen effusion cells. In situ reflection high energy electron diffraction (RHEED) was used to assess crystalline quality. Post-growth structural characterization was performed via X-ray diffraction (XRD) and high annular dark field scanning transmission electron microscopy (HAADF-STEM).

In situ RHEED images suggested the ScxAl1-xN layers remained epitaxial throughout the growth and the subsequent GaN layers retained their hexagonal crystal structure. Atomic force microscopy (AFM) images showed surfaces with an RMS roughness of less than 2 nm, with hillocks related to potential extended defects. However, the defects generated in the ScxAl1-xN layers were not sufficient to disrupt the nucleation of wurtzite GaN. HAADF-STEM measurements corroborated these findings and confirmed that a growth interrupt to desorb excess Ga prevented atomic-level chemical mixing between GaN and ScxAl1-xN, leading to sharp interfaces. Growth using the higher purity Sc source showed higher structural quality, evidenced by comparative XRD. This study highlights the importance of growth conditions and source material selection for the optimization of epitaxial ScxAl1-xN-GaN heterostructures.

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TF-Contributed On Demand-25 Deposition of Large-Grained Polycrystalline Aluminum Nitride at Low Temperature via Bias-Enhanced Atomic Layer Annealing, ***Aaron McLeod**, S. Ueda, A. Kummel,* UC San Diego

Electrically insulating heat spreading materials are needed in integrated circuits to realize for three-dimensional integration and for all high power RF devices. Potential materials of interest include aluminum nitride, diamond, and hexagonal boron nitride, though only aluminum nitride is synthetically practical at low temperature and isotropically conducting. A method has been developed to deposit crystalline aluminum nitride at temperatures below 450 °C on non-lattice matched substrates (silicon) using bias enhanced atomic layer annealing. This technique is unique in its addition of a plasma treatment step to the end of each traditional atomic layer deposition cycle, in which ion bombardment increases surface adatom energy and promotes crystallization. Tris(dimethylamido) aluminum and anhydrous hydrazine are used as precursors. The crystalline orientation of the deposited aluminum nitride can be controlled by altering the kinetic energy of the incident ions. This is accomplished by altering the substrate bias and gas identity: biases of -10V, -25V, and -40V were investigated for Ne, Ar, and Kr plasmas. Ion flux across all conditions was kept constant at ~0.3mA/cm^2 by adjusting the plasma source power. The composition and crystallinity of the films are analyzed using in-situ x-ray photoelectron spectroscopy (XPS) and ex-situ grazing incidence x-ray diffraction (GI-XRD). Depositions of 40 nm thick films were performed on Si(111) and SiC substrates. On Si(111), optimal crystallization is achieved using Ar at -25V bias, producing a film with selective (200) orientation and an average crystallite size of 27 nm. Neon and Kr produced films with preferential (002) orientation, though average crystallite sizes were less than 11 nm for all conditions. These results highlight that the crystallization effects afforded by this technique are a tradeoff between ion induced mobility and ion induced damage (embedding and dislocations) and is not a thermal effect.

TF-Contributed On Demand-28 Exploiting Fixed Charge to Control Schottky Barrier Height in Si|Al_2O_3|MoO_x- Based Tunnel Diodes, ***Ben Garland**, B. Davis, N. Strandwitz,* Lehigh University

Carrier selective contacts have become one of the leading advancements in photovoltaics with the most efficient structures exceeding 26% conversion efficiency. Selective carrier conduction implies that one type of charge carrier is preferentially collected at an electrical contact. Carrier selectivity increases the efficiency of solar cells by reducing recombination at metal contacts and avoiding highly doped emitter layers. Popular selective contact materials are often transition metal oxides (TMOs) due to high optical transparencies and large work functions that are useful for hole selective contacts to silicon. In contrast to previous articles, recent studies have indicated that the interface of p-type silicon and the molybdenum oxide (MoO_x) exhibits a significant Schottky barrier that decreases the efficiency of hole-selective contacts by impeding majority carrier hole collection. To alleviate this issue, atomic layer deposited (ALD) alumina (Al_2O_3) might be added between Si wafer and MoO_x with the expectation to generate a negative interface fixed charge (N_f) after annealing, decreasing band bending. ALD Al_2O_3 also has the ability to passivate interface traps with diffusion of precursor hydrogen during annealing. In this work, we hypothesize that insertion of a tunneling ALD Al_2O_3 layer between MoO_x and p-type Si will enable Schottky barrier height (ϕ_{bh}) minimization that is tunable with N_f, enabling a high efficiency hole-selective contact.

Since there should not be quantifiable N_f in tunneling Al_2O_3 using capacitance-voltage (C-V) analysis, non-tunneling n-Si|Al_2O_3|Al MOSCAP structures were used to determine ideal processing for maximum negative N_f. The ALD growth of Al_2O_3 utilized trimethylaluminum and H_2O at 4 deposition temperatures. Half of the samples were annealed at 425°C in a nitrogen atmosphere prior to the application of Al contacts. After N_f quantification, p-Si|Al_2O_3|MoO_x|Al tunnel diodes with thin (~1 nm) as-deposited and annealed Al_2O_3 layers were fabricated to determine ϕ_{bh}. Current density-voltage-temperature (J-V-T) and Mott-Schottky 1/C^2-V measurements were used to establish a range for ϕ_{bh}. Both methods showed that the as-deposited tunneling Al_2O_3 diodes had a higher ϕ_{bh} compared to the diodes with annealed tunneling Al_2O_3, and therefore also supported the existence of a ϕ_{bh} at the Si|MoO_x interface. Future work will involve using larger barrier height diodes using n-Si to more accurately calculate ϕ_{bh} and confirm or reject the phenomenon observed.

TF-Contributed On Demand-31 Development of Reusable Hydrogel for Fabric-based Bioelectrodes via initiated Chemical Vapor Deposition (iCVD), ***S. Zohreh Homayounfar**, S. Rostaminia, A. Kiaghadi, D. Ganesan, T. Andrew,* University of Massachusetts Amherst

There is a significant interest in measuring biopotential signals (such as ECG and EOG) unobtrusively via novel textile-based electronics. Herein, electrodes are the interface who receives the charges in the ionic form from the body and injects them as electrons through wires. A fundamental challenge to be addressed to reliably measure biopotential parameters with fabric-based electrodes is whether we can design an electrode that has the signal quality of traditional wet electrodes and the comfort of dry electrodes. The crucial role of a hydrogel in an electrode, specifically in reducing the motion artifact, is undeniable. However, fabricating a hydrogel that can be stably grafted to the underneath plate and, maintains a constant baseline ion concentration, and most importantly, can be fully recovered after being dried out is still a great challenge among scientists. In this study, we developed a mechanically stable hydrogel as the electrolyte on our bioelectrode by taking advantage of initiated Chemical Vapor Deposition (iCVD). Our first-of-its-kind hydrogel electrodes successfully address all known drawbacks of conventional “wet” electrodes, in addition to affording high signal to noise ratio during long-term data acquisition, displaying wash-stability, breathability, no skin irritation, and being capable of further miniaturization for embedding into any wearable platforms.

TF-Contributed On Demand-34 On Achieving Single-Phase Crystalline Gallium Oxide Thin Films at Low Thermal Budgets, ***Elham Rafie Borujeny**, K. Cadien,* University of Alberta, Canada

Gallium oxide (Ga_2O_3) is an emerging wide bandgap material (bandgap > 4.0 eV) with a large breakdown field which make it a suitable candidate for integration in electronic and optoelectronic devices. Crystalline forms of gallium oxide, specially in thin film form, are required for realization of such devices that can complement the superior properties of other wide bandgap semiconductors in use today (such as gallium nitride (GaN)). However, Ga_2O_3 thin films can currently be obtained on very limited substrates (namely, Ga_2O_3 and sapphire) in specific process conditions or at high temperatures.

In this work, we demonstrate novel deposition strategies to deposit high-quality single-phase Ga_2O_3 films at low temperatures on non-native substrates as a key enabling technology for implementation of Ga_2O_3 in next-generation electronic devices. Taking advantage of the unique crystallographic features of Ga_2O_3, we propose a universal and robust approach to control the crystallinity of Ga_2O_3 thin films in situ and achieve single-phase α-Ga_2O_3 films at low thermal budgets. We also show that, based on energetics considerations, it is possible to alter the population of metastable gallium oxide polymorphs in the films and design deposition processes that can achieve substantially single-phase β-Ga_2O_3 on non-native substrates. All the processes discussed in this work are performed at low temperatures (i.e., temperatures that are hundreds of degrees lower than the temperatures commonly in use today for growth of crystalline gallium oxide in either bulk or thin film forms); therefore, they provide new opportunities in simultaneously achieving energy efficiency and high performance in Ga_2O_3 electronics.

TF-Contributed On Demand-37 Gallium Oxynitride Thin Films with Tunable Properties for Electronic and Photonic Applications*, Elham Rafie Borujeny*, *K. Cadien,* University of Alberta, Canada

GaN is a semiconductor with superior properties including stability at high temperature, high thermal conductivity, high electron mobility, and high breakdown voltage compared to Si and GaAs. These outstanding properties, which make GaN the frontrunner material in power electronics applications (such as energy-efficient inverter circuits) as well as in photonics applications (such as LEDs), strongly depend on GaN crystal structure. In this work, we propose strategies for incorporation of oxygen in the crystal structure of GaN at low temperature and show that these strategies can be used to tune the structure as well as the properties of the resulting films. We obtain gallium oxynitride films with tunable lattice constant, bandgap, and resistivity that can be used in both electronic and optoelectronic devices either as the active layer of the device or as a passive component used to adjust the properties and the performance of such devices.

The results of this work enable growth of gallium oxynitride thin films, with superior material properties offered by ALD, not only with potential applications as high-performance materials in reducing energy consumption but also with an energy-efficient fabrication process.

TF-Contributed On Demand-40 Atomic Layer Deposited Metal Oxide Bilayers for Metal-Insulator-Semiconductor Photovoltaics*, Benjamin Davis*, *N. Strandwitz,* Lehigh University

The use of metal-insulator-semiconductor (MIS) tunnel diodes as photovoltaics (PVs) relies on the Schottky barrier between the metal and semiconductor, which induces band bending in the semiconductor absorber allowing for efficient separation of electrons and holes. In the years following early MIS PV research in the 1970s and 1980s, the advent of atomic layer deposition (ALD) has provided a tool for enhanced control of ultrathin film deposition. One method to potentially improve MIS PV performance is the use of ALD oxide bilayers as tunnel insulators. Oxides with different oxygen areal densities have been demonstrated to form interfacial dipoles, manipulating the Schottky barrier. Previous studies have only explored the impact of dipoles between a single ALD oxide and interfacial SiO_x. The present work combines two ALD oxides, one (AlO_x) with oxygen areal density higher than that of SiO_x and another (LaO_x) with oxygen areal density lower than that of SiO_x according to literature. It has been hypothesized that the greater oxygen areal density difference would result in a greater impact on the Schottky barrier. It is demonstrated that, compared to AlO_x alone, an ALD LaO_x/AlO_x stack increases the average n-Si/Ni Schottky barrier height from 0.63 to 0.70 eV, and the average p-Si/Al barrier height from 0.81 to 0.90 eV. In all cases, LaO_x was the oxide in direct contact with the Si substrate. The observation that the barrier height increases for both substrate types suggests that the effect is due to the ability of LaO_x to depin the Fermi level rather than an interfacial dipole.

TF-Contributed On Demand-43 Fabrication of Nanoscale Multilayered Thin-Film Thermoelectric Materials and Devices*, Lauren Williams*, *A. Henderson, R. Miller, B. Whitaker, R. Glenn, Z. Xiao,* Alabama A&M University

We report the growth of nanoscale multilayered thermoelectric thin films and fabrication of integrated thermoelectric devices for high-efficiency energy conversion and solid-state cooling. Nano multilayered Bi_2Te_3/Sb_2Te_3, Sb/Sb_2Te_3 and Te/Bi_2Te_3 thermoelectric thin film materials were grown using the e-beam evaporation. The thin films were prepared with 100 to 150 layers, where each layer is about 3 to 5 nm thick. Integrated thermoelectric devices were fabricated with the nanoscale multilayered thin films using the clean room-based microfabrication techniques such as UV lithography. Plasma-enhanced atomic layer deposition (PE-ALD) was used to grow zirconium dioxide (ZrO_2) as the insulation layer in the device fabrication. X-ray diffraction and high-resolution tunneling electron micrograph (HR-TEM) were used to analyze the nanoscale multilayered thin films. SEM was used to image and analyze the fabricated devices. The thermoelectric characteristics of the fabricated devices were measured and analyzed, and the effect of the nanoscale multilayer structures on the thermoelectric efficiency was investigated.

TF-Contributed On Demand-46 Influence of Gold Layer Thickness on the Metal-Induced Crystallization Behavior of Ge Thin Films*, Narin Sunthornpan*, *K. Kimura, K. Kyuno,* Shibaura Institute of Technology, Japan

Germanium (Ge) is one of the most intensively studied semiconductor materials because of its superior properties such as higher carrier mobility and smaller energy bandgap compared to silicon (Si). These properties are advantageous in applications such as thin-film transistor, solar cell, next generation MOSFET, etc. Nevertheless because of its higher cost, fabricating high quality crystalline Ge thin film on glass and plastic substrates is a key to realize these devices. Metal-induced crystallization (MIC) technique by gold (Au) catalyst is one of the promising choices to crystallize Ge films because of its low crystallization temperature. Nevertheless, further knowledge about the crystallization mechanism is needed to optimize the crystallization process. To this end, the influence of Au layer thickness dependence on structural and electrical properties of Ge films crystallized by MIC technique has been investigated in this study.It is found that a Ge thin film (30nm) starts to crystallize at a lower temperature for thinner Au layer thickness. A higher (111) orientation is also achieved for thinner Au layer thickness and a hole mobility as high as 50 cm^2/Vs is achieved for Ge thin films crystallized by a 6nm Au layer at 220 °C, which is low enough to fabricate electronic devices on plastic substrates such as polyimide.

Au films ranging from 6 to 23 nm were prepared by RF magnetron sputtering process on Si wafer with 100 nm thermally grown oxide (SiO_2) layer. Subsequently, Ge films (30 nm) were deposited on these Au films. To crystallize Ge film, all films were annealed with temperatures ranging from 100 to 220 °C under N_2 ambient. Structural properties were examined by X-ray diffraction (XRD), Raman spectroscopy and electron backscattered diffraction (EBSD). It is found that Ge crystallization starts at a temperature as low as ~140°C, which decreases slightly as the Au layer thickness decreases. Moreover, higher Ge (111) orientation was achieved for thinner Au layer thickness, which was confirmed by XRD and EBSD observation. From the Hall effect measurement, a p-type behavior and a hole mobility as high as 50 cm^2/Vs was obtained for Ge thin film crystallized by annealing a Ge(30nm)/Au(6nm) bilayer at 220 °C. Transistor action was also successfully demonstrated by using these films as channel layers. These findings will open up the possibility to apply MIC technique with smaller Au consumption to fabricate thin-film semiconductor on various inexpensive plastic substrates.

TF-Contributed On Demand-49 *In Situ* Reflection High Energy Electron Diffraction in Atomic Layer Deposition for Monitoring Epitaxial Transformations*, Alexandra Howzen*, *N. Strandwitz,* Lehigh University

The maximum amount of thermal energy available during atomic layer deposition (ALD) is generally determined by the decomposition temperature of the precursors and also sets the maximum temperature in the "ALD window".This maximum temperature in some cases limits the structural perfection and extent of crystallization in resulting films.Intermittent annealing during the film growth in between ALD chemical exposures has been explored previously and shown to increase density and quality of ALD films.[1] However, without direct monitoring of one or more of the physical properties of the films, it can be difficult to determine the nuances of film transformation, such as crystallization temperature, surface roughening, and dependence on gas ambient.

In this work we integrate reflection high energy electron diffraction (RHEED) into a home-built ALD system to monitor structural and morphological transformations during ALD growth and thermally-induced structural transformations.RHEED is a surface sensitive diffraction technique that utilizes high energy (> 10 keV) electrons at a glancing angle, and is most commonly utilized in molecular beam epitaxy and pulsed laser deposition systems. The relatively high pressures associated with ALD are incompatible with RHEED due to filament instability and resulting short electron mean free path within the chamber, necessitating either 1) differential pumping on the electron gun and a short path length between the electron gun and phosphor screen or 2) a pump down to high vacuum conditions. In addition to describing the system design, flow, and thermal modelling; we will show initial results of the deposition and annealing of ultrathin films (1-20 ALD cycles) focusing on transformations of polymorphic Ga_2O_3. The integration of RHEED with ALD offers a slow-motion picture of traditional epitaxial growth techniques by decoupling the deposition and crystallization steps with simultaneous monitoring of the surface structure.

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TF-Contributed On Demand-52 Sputter Deposition of Al_3Sc Films for Microelectronics Fabrication

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Aluminum scandium ($Al_{1-x}Sc_x$) metal films are explored for their use in semiconductor processing as electrical leads for high temperature applications and etch resistant characteristics. When deposited at elevated temperatures or subsequently annealed at temperatures ≥ 600°C, the resistivity of the $Al_{1-x}Sc_x$ films decreases, with substantial decreases seen in films that had a lower deposition temperature. The crystallographic texture of the Al_3Sc phase that is formed during deposition is {111}-oriented. The template used for Al_3Sc deposition is shown to be critical in its {111} crystallographic alignment as well as the deposition temperature. The lowest as-deposited resistivity value for the 100-nm Al_3Sc metal film deposited at 450°C was ~18 μΩ-cm, with subsequent anneals resulting in an improvement to ~10 μΩ-cm. Characterizing annealed films at different temperatures with transmission electron microscopy (TEM) and X-ray diffraction (XRD) show the amount of the Al_3Sc phase increases with higher annealing temperature. Therefore, the formation of Al_3Sc is suspected of being the key factor that leads to reduce resistivity. The ability for this metal to withstand anneals at 600°C while resulting in lower resistivity suggest that it can operate at these temperatures and aid in extending the operating temperature of piezoelectric devices beyond 500°C. Additionally, given the introduction of Sc into Al, this metal film behaves similarly to piezoelectric $Al_{1-x}Sc_xN$ when using an inductively coupled plasma etch that uses Cl_2 and BCl_3 chemistries. The resulting etch rate for $Al_{0.80}Sc_{0.20}$ films was ~25 nm/min, which is ~12x lower than the etch rate for AlN and on par with Pt metal. Dry etch experiments show that $Al_{0.80}Sc_{0.20}$ metal is resistant to Cl-based chemistries with Sc metal being exceptionally resistant, thus, $Al_{1-x}Sc_x$ films can show strong etch resistance across the entire Al-Sc system. Given the etch resistant characteristics of $Al_{1-x}Sc_x$, this metal film can serve as either an etch stop or an etch mask in microelectronics fabrication that exhibits low resistivity values and is CMOS-compatible.

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TF-Contributed On Demand-55 Vertical Heterostructures of Two-Dimensional Transition Metal Chalcogenides by Atomic Layer Deposition

__Saravana Balaji Basuvalingam__, M. Bloodgood, M. Verheijen, W. Kessels, A. Bol, Eindhoven University of Technology, The Netherlands

2D transition metal chalcogenides (TMCs) such as dichalcogenides (TMDCs; MX_2) and trichalcogenides (TMTCs; MX_3) have gained a lot of attention for their unique optoelectronic properties. Lately, fabricating vertical heterostructures of 2D TMDCs has gained significance over the heterostructure of 3D materials due to their clean interfaces. Stacking different 2D materials on top of each other continues to opens up unique functionalities and application prospects[1]. The 2D TMDC heterostructures exhibit large potential for optoelectronic devices, but the ability to fabricate them over a large area (wafer scale) is a persisting challenge. Fabricating 2D heterostructures conformally over a 3D structure has also become a key challenge as the complexity of device structures keeps increasing. Additionally, 2D heterostructures of TMDC-TMTC have not yet been explored experimentally.

In this work, we demonstrate that challenges associated with 2D heterostructures fabrication in commonly used methods; such as process scalability, uniformity, control over individual material thicknesses, conformality and processing temperatures can be overcome using atomic layer deposition (ALD). Lately, ALD has become of significance for the synthesis of various 2D TMDCs[2] and TMTCs[3]. Here, we also show that ALD is favorable for the fabrication of 2D heterostructures consisting of both TMDCs and TMTCs.

We report on the synthesis of 2D TMDC heterostructures in the form of TiS_x-NbS_x using ALD at ≤300 °C. First, we developed ALD processes for both TiS_x and NbS_x independently using metal-organic precursors and H_2S gas as coreactant. A 5-layer TiS_x-NbS_x heterostructure with varied individual layer thickness was fabricated to demonstrate the ability to precisely control the thickness of the individual TMDC layers by ALD. In addition to TMDC heterostructure formation on a planar substrate, the conformal growth on a 3D substrate by ALD was demonstrated by depositing the same 5-layer TMDC heterostructure on a nanowire array. Furthermore, this work also shows phase-controlled growth of NbS_3 on NbS_2 yielding NbS_2-NbS_3 TMDC-TMTC heterostructures. The phase-control between NbS_2 and NbS_3 was obtained by modulating the H_2S:H_2 ratio in the coreactant at a constant deposition temperature of 300 °C.The current study exhibits the advantages of ALD for the scalable synthesis of 2D heterostructures on 3D structures with precise thickness control at low temperatures. This work will open new avenues for both ALD and 2D TMCs in terms of nano device fabrication.

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TF-Contributed On Demand-58 Multi-Stimuli Responsive Nanorods for Artificial Skin Applications

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The work summarized in this abstract presents a multi-stimuli responsive sensor for artificial skin applications. The sensor can detect surrounding changes in temperature, humidity and force. The developed design consists of a hydrogel core, responsive to temperature and humidity changes; and a piezoelectric shell for force sensing. Swelling of the hydrogel core, in response to stimuli, mechanically strains the piezoelectric shell and a measurable electric charge is generated. The two materials are combined into core-shell nanorod structures, using state-of-the-art vapor-based deposition techniques. These deposition techniques provide control over material's mechanical, optical and electrical properties in addition to film's conformity and uniformity. Moreover, the core-shell nanorods are deposited into a nanostructured UV-curable resin, providing mechanical stability against structural collapse.

- Synthesis of hydrogel core: humidity and temperature responsive hydrogel, Poly-N-vinylcaprolactam (pNVCL), is synthesized using intitiated chemical vapor deposition (iCVD). The dry vapor-phase technique gives control over the lower critical solution temperature (LCST), amongst other material properties.(1) Tailoring the hydrogel's LCST defines response over a specific temperature range.
- Synthesis of piezoelectric shell: piezoelectric zinc oxide is synthesized using plasma-enhanced atomic layer deposition (PE-ALD).In PE-ALD, substrate temperature defines the deposited film's crystalline properties. A combination between (100) and (002) crystallographic orientations gives control over zinc oxide's piezoelectric properties. In this work, piezoelectric zinc oxide layer with combined (100) and (002) preferential orientation is deposited at low temperatures, which is advantageous for when flexible substrates, such as PET, are used.(2)
- Nanostructuring of UV-curable resin: The multi-stimuli responsive core-shell nanorods are deposited into nanostructured UV-curable polyurethane acrylate (PUA) resin functioning as a template. Patterning is achieved using UV nanoimprint lithography (UV-NIL).

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TF-Contributed On Demand-61 Towards Area-Selective Deposition: Nucleation and Initial Growth of ZnO During Plasma-Enhanced ALD on Polymer Thin Films

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Area-selective atomic layer deposition (AS-ALD) has become a hot topic in the field of nanofabrication for combining self-aligned patterning with precise thickness control and high conformality of the resulting thin films. Over the past years, area-selective growth has been successfully demonstrated for a variety of materials. However, to date, most processes have focussed on the selective deposition on inorganic-inorganic or inorganic-organic substrate combinations employing thermal ALD.

It is our aim to extend area-selective deposition processes to polymer-polymer patterns, thus accessing new applications fields such as organic electronics or nanodevice fabrication based on 2-photon polymerization. The use of plasma-enhanced ALD (PE-ALD) instead of thermal ALD provides a completely new approach towards area-selective growth by using the etching effect of the plasma on the polymer substrates to achieve different growth delays.

As an essential step towards area-selectivity, nucleation and initial growth of ZnO on two different vapor deposited homopolymer thin films - ethylene glycol dimethacrylate (EGDMA) and hydroxyethylmethacrylate (HEMA) - are investigated using in-situ spectroscopic ellipsometry. This is the first time that an initial growth study is conducted for PE-ALD on polymer thin films.

Our results show that film formation is a consequence of two competing processes: ZnO ALD growth and plasma etching of the polymer substrates. During the initial ALD cycles, polymer etching dominates, resulting in an overall decrease in thickness. At a certain point, ZnO growth takes over and the regime of normal ALD growth behaviour is entered. This etching-induced growth delay is found to depend both on the oxygen plasma power and the type of polymer. At 30 W plasma power, ZnO growth starts to dominate after 3 and 5 ALD cycles for EGDMA and HEMA respectively with a total polymer thickness loss of less than 2 nm. At 60 W, stronger etching (3.2 and 3.8 nm/10 s plasma pulse) leads to higher growth delays of 13 and 20 cycles. This material-dependent difference in growth delay is exactly what is needed for area-selective growth. Raising plasma power further results in higher etching rates (5.7 and 8.3 nm/plasma pulse at 100 W) but does not further increase the growth delays. The resulting ZnO films (20 nm thick) are very smooth with roughness values ranging from 50 pm at 30 W plasma power to 350 pm at 100 W.

Our work provides vital knowledge about the initial growth of ZnO during PE-ALD on polymer thin films and illustrates a novel approach towards area-selective deposition by exploiting material-dependent growth delays induced by plasma etching.

TF-Contributed On Demand-64 Process Optimization in Atomic Layer Deposition Using Machine Learning

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Process development and process optimization are ubiquitous, resource-intensive tasks in thin film research and development. The goal of these activities is to find the set of process parameters (e.g. temperature, pressure, and flow) that maximize film quality at minimal cost. Typically, this is accomplished by coating a substrate (e.g. a silicon wafer) under a given set of conditions, measuring the film properties ex situ, and adjusting the conditions to improve the film quality. This activity can consume significant time and resources, especially if an additional goal is to achieve uniform films across a large substrate. Process development can be accelerated and economized using in situ measurements. For instance, quartz crystal microbalance (QCM) measurements can be employed to monitor film thickness in real time as the deposition conditions are varied. However, this still requires the careful attention of a skilled operator to make informed choices based on experience and intuition. An alternative strategy is to use machine learning (ML) to analyze the QCM data in real time and adjust the growth conditions based on an algorithm. To explore this possibility, we used ML to optimize the atomic layer deposition (ALD) of Al_2O_3 with trimethyl aluminum (TMA) and H_2O in a viscous-flow tubular reactor using in situ QCM measurements. We initially developed the ML code using simulated QCM data generated by a 1-D model of ALD transport and reaction. This allowed us to tailor the algorithm to ensure saturation of the TMA and H_2O ALD reactions and to converge efficiently on the optimal dose and purge times. We examined several ML algorithms including Bayesian optimization, physics-inspired optimization, and random optimization. An additional benefit of these simulations was that we could explore the effects of non-ideal behavior such as a CVD component to the surface reactions and strong interaction between the reaction products and the surface. Next, we interfaced the ML code to our ALD system and allowed the algorithm to optimize the TMA and H_2O timings. We observed rapid convergence, as predicted by our simulations, and found that the ML algorithm was capable of adapting to variations in the initial conditions such as the precursor partial pressures and the carrier gas flow rate. We are now building an array of QCM sensors to measure the thickness simultaneously at 10 locations along our flow tube, and we hope to report on ML opimization of thickness and uniformity using this array.

TF-Contributed On Demand-67 Influence of Precursor Density and Conversion Time on Vapor Deposited Oriented ZIF-8 Thin Films

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Solvent-free methods for synthesis of metal organic frameworks are currently on the rise, with the aim of facile processing and access to new application fields. These requirements are met by MOF-CVD – a two-step chemical vapor deposition process, that allows for the delivery of high-quality, homogeneous thin films of zeolitic imidazole framework 8 (ZIF-8) from ZnO[1]. By subjecting ultrathin (100)-oriented ZnO layers deposited via plasma-enhanced atomic layer deposition (PE-ALD) to a 2-methylimidazole vapor, homogeneous ZIF-8 thin films are obtained with controlled thickness.

While all forms of ALD offer precise thickness control, and conformality for thin film deposition in a solvent-free environment, PE-ALD offers the additional advantage of tuning the substrate temperature over a broad range, from room temperature to over 200°C by utilizing a reactive plasma species as the co-reactant. This parameter influences amongst others the preferential crystal orientation of our ZnO thin films, leading to a preferred (100)-orientation by keeping the substrate at room temperature[2]. To the best of our knowledge, this study is the first to employ PE-ALD for MOF synthesis via the MOF-CVD process.

To gain better control over the novel deposition technique, the impact of conversion time in combination with different densities (4.6 g/cm^3 and 5.2 g/cm^3) and thicknesses (1 to 10 nm) of the ZnO precursor onto the resulting ZIF-8 thin films was investigated.

X-ray diffraction studies reveal that ZIF-8 was successfully synthesized and show a powder-like structure together with a preferred (100) or (111) orientation of ZIF-8 crystals, depending on precursor thickness and density, growing more prominent with longer conversion times. The onset of crystallization occurs after mere 20 min of conversion time for the less dense precursor compared to after 40 min for the denser precursor. Also, ZIF-8 thickness and roughness increase with longer conversion times. The final thickness depends on the precursor thickness and precursor density, increasing up to 16-fold during the conversion for the less dense precursor.

Our results provide vital knowledge about the link between deposition parameters of PE-ALD deposited ZnO and properties of the resulting ZIF-8 thin films, namely crystallographic orientation, thickness, coverage and roughness, thus making it possible to tailor them towards specific applications.

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TF-Contributed On Demand-70 Modeling the Coalescence and Morphology as a Function of the Nucleation and Growth Rates

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State-of-the-art integrated circuits require the deposition of few nm-thick, ultra-smooth, and pinhole-free metallic films in the device architecture, e.g., as diffusion barriers. However, CVD growth often begins from a collection of islands that become many nm tall before the entire substrate surface is covered; such films are far too rough to meet device requirements and may contain pinholes. This poor morphology occurs when the areal density of film nuclei is small relative to the growth rate on the nuclei. We previously reported two methods to dramatically improve the outcome: treating the surface to increase the density of nuclei that form at the start of film growth or using an inhibitor to reduce the film growth rate without reducing the rate at which additional nuclei can form. We have shown that a combination of these approaches affords a continuous film of Co on SiO2 that is 2 nm thick with a root mean square roughness of only ~ 0.3 nm.

Here, we use Monte-Carlo modeling to examine the role of three parameters on the morphology of ultra-thin films: the areal density of initial nuclei, the rate at which additional nuclei form, and the rate at which islands grow after nucleation. We report the evolution of the accumulation rate of film between initial nucleation and final coalescence and the corresponding surface roughness. We identify a power law relationship that connects the roughness at coalescence with the ratio of the areal nucleation rate to the growth rate on the nuclei. We also derive an analytical model, based on Poisson point statistics, that independently predicts the same power law dependence. We then compare model results with experimental data for HfB2 growth by CVD. These models are in good overall agreement with experimental data. However, the existence of substrate-dependent effects indicates that additional mechanisms, e.g., those driven by surface diffusion, modify the results obtained using the three parameters alone.

**TF-Contributed On Demand-73 Tunable ALD Infiltration into Ultra-High-Aspect-Ratio Aerogels Enabled by Process Modeling for High-Temperature Solar Thermal Applications*, Andrew J. Gayle*, *Z. Berquist, Y. Chen, 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 helps enable their use in fields such as concentrated solar thermal (CST), catalysis, and filtration. In particular, SiO2 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 coat SiO2 aerogel monoliths (AMs) with aspect ratios >60,000:1 [1]. In order to minimize precursor waste during the long diffusion times necessary to conformally coat 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. Building on previous work by Gordon [2] and Yanguas-Gil [3], 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 coating 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. After deposition, the AMs showed enhanced infrared light absorption while maintaining high visible light transparency after only one cycle of ALD Al2O3. The ALD-coated AM also showed improved resistance to structural degradation at elevated temperatures, likely due to stabilization of the SiO2 nanoparticle surface. These changes may be due to the formation of a ternary Al-Si-O phase at the interface between the SiO2 backbone and deposited Al2O3 film, as shown using XPS measurements. This combination of properties makes the ALD-coated AMs a promising transparent insulating material (TIM) for CST applications.

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**TF-Contributed On Demand-76 Ethanolamines as Bath Additive in Copper Electroless Deposition: Effect on Film Adhesion and Nanowire Formation*, Jevalyne Vienes*, *A. Walker,* University of Texas at Dallas

Electroless deposition (ELD) is one of the most commonly employed techniques for the deposition of metals on organic substrates. Although it is widely used, there has been few studies on the effect of bath additives on deposition. In this paper we investigate the effect of primary, secondary and tertiary amines on the adhesion of copper films and formation of copper nanowires using ENDOM. We employ optical microscopy, secondary electron microscopy, x-ray photoelectron spectroscopy and time-of-flight secondary ion mass spectrometry. Two model organic substrates are employed: -OH and -CH_3 terminated self-assembled monolayers (SAMs). These were chosen because they exhibit hydrophilic and hydrophobic properties, respectively. Our data show that both the concentration and type of ethanolamine affect the deposition. Using monoethanolamine, the copper deposit does not strongly adhere to the SAMs. Further, the data also show that the copper film is more adherent to the -OH terminated SAMs than -CH_3 terminated SAMs. We attribute these effects to the interaction of the polar hydroxyl terminal group with the ethanolamines, and further that the ethanolamines provide nucleation sites for the copper deposit on the organic substrates. Our data suggest that monoethanolamine and triethanolamine interact with the SAMs via the amine terminal group while diethanolamine lies flat on the SAM substrates. We then exploit these effects to deposit copper nanowires at the interface of -CH_3 and -OH terminated SAMs using electroless nanowire deposition on micropatterned substrates (ENDOM). We show that the formation rate of the nanowires can be increased, or decreased, by using different ethanolamines. We demonstrate that nanowires form using monoethanolamine and triethanolamine but diethanolamine.

**TF-Contributed On Demand-79 Plasma Enhanced Atomic Layer Deposition of WO_X Using a Wide Temperature Stability Precursor*, Kamesh Mullapudi,* *K. Holden, J. Peterson,* Oregon State University*; R. Kanjolia, D. Moser, C. Dezelah,* EMD Performance Materials*; J. Conley Jr.,* Oregon State University

Tungsten oxide (WO_3) has garnered interest lately for its use in smart windows, gas-sensors, and as a potential candidate for emerging neuromorphic memories. Microelectronics applications require films of high electrical quality with excellent conformality, uniformity, and thickness control for which atomic layer deposition (ALD) is the method of choice.

Early thermal ALD reports of WO_3 films employed the use of halides which resulted in self-etching by reaction byproducts and carbonyl precursors with narrow ALD windows.[1,2] More recent work has focused on metal-organic chemistries and plasma-enhanced ALD (PEALD), which provides benefits such as lower deposition temperatures and wider ALD windows. Examples include $WH_2(iPrCp)_2$ & direct O_2 plasma at 300°C, $W(tBuN)_2(Me_2N)_2$ & direct O_2 plasma with a constant growth per cycle (GPC) window between 215-286°C, and $WH_2(Cp)_2$ & remote O_2 plasma with a constant GPC window between 200-300°C.[3,4] Both $W(tBuN)_2(Me_2N)_2$ and $WH_2(Cp)_2$ showed signs of decomposition above 300ºC, limiting their use at higher temperatures.[5,6] There remains a need for a precursor with a wider temperature range compatibility.

In this work we report PEALD of WO_3 using a novel metal-organic tungsten precursor [bis(tert-butylimido)bis(trimethylsilylmethyl)tungsten(VI), $W(CH_2Si(CH_3)_3)_2(CN(CH_3)_3)_2$ or WSN-4] with remote O_2 plasma in a Picosun R200 reactor. Using a 2/15/60/30 sec WSN-4/N_2/O_2 plasma/N-$_2$ pulse sequence, GPC decreases from 1.0 to 0.4 Å/cycle as the growth temperature increases from 120 to 285°C, becoming relatively constant between 285 and 370°C. The higher growth temperatures are accompanied by an increase in optical refractive index and a slight reduction in bandgap (Fig. 1). Self-limiting growth was observed even at 200°C (Fig. 2 & 3) indicating the low-temperature compatibility of the process. Grazing angle x-ray diffraction (GI-XRD) reveals that 12 nm thick films deposited at 200°C are amorphous, while post-deposition isochronal (60 min) O_2 annealing at 600°C produces crystallization into the triclinic phase of WO_3 with an estimated grain size of ~30 nm (Fig. 4 and SEM image inset).

Further details on WSN-4 properties, nucleation behavior on BEOL metals such as TiN and TaN, film density, stoichiometry, and electrical properties of ALD WO_3 will be discussed at the meeting.

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**TF-Contributed On Demand-82 Molecular Layer Deposition of Phosphane-Ene Polymer Films*, Sean Barry,* Carleton University, Canada*; P. Ragogna,* University of Western Ontario, Canada*; P. Gordon,* Carleton University, Canada*; C. McGuiness,* Solvay

Molecular layer deposition of organic polymer thin films has become a burgeoning research field, and the types of completely organic thin films continue to grow: examples of nitrogen-containing polyimides polyamides, oxygen-based polymers like PEDOT, and sulfur-containing thiol-enes all expand the application space for MLD polymer films.

Phosphane-enes are phosphorus-rich, using a cross-linking alkene and a wide variety of phosphines to synthesize a family of highly tunable and structurally diverse versatile polymers. These have previously been fabricated in the solution phase using photo-induced polymerization. This work reports the gas-phase MLD of a tetravinylsiloxane-based phosphanene using isobutyl phosphine.

The MLD employs an A-B-C pulse sequence: a 0.1 s phosphine pulse, held for 149 s to allow full monolayer formation, 60 s Ar plasma pulse, followed by a 1.0 s TTC pulse held for 149 s to allow full reaction with the phosphine monolayer. The process was run at 40 °C and 600 W plasma power gave a growth per cycle of 0.8 Å.

This presentation will detail the suspected growth mechanism and characterization of the film by SEM, AFM, EDS, and XPS. The polymer selectively grows on hydroxylated surfaces; selectivity studies between metal surfaces and hydroxylated silicon surfaces will also be presented.

TF-Contributed On Demand-85 Atomic Layer Deposition of HfO_2 on SiO_2: Evidence for a Bimolecular Reaction Mechanism in the Initial Metal Half-Cycle, *P. Shayesteh,* Lund University, Sweden*; R. Tsyshevsky,* University of Maryland*; A. Head,* Brookhaven National Laboratory*; J. Gallet,* Sorbonne Université and Synchrotron SOLEIL, France*; F. Bournel, F. Rochet,* Sorbonne Université, France*; M. Kukla,* University of Maryland*;* ***Joachim Schnadt,*** Lund University, Sweden

Today, atomic layer deposition (ALD) [1] is among the most important methods for thin film growth [2], especially in semiconductor device technology, but increasingly also for, e.g., solar energy conversion, catalysis and energy storage materials. Ideal ALD processes exhibit excellent dimension control in the direction perpendicular to the surface onto which the thin film is deposited. The very high degree of control derives from a well-defined surface chemistry that is based on the saturative adsorption and surface reaction of the ALD precursors. Real ALD processes deviate, however, from the idealised reaction mechanisms [3,4]. This results in deviation from ideal film growth and loss of deposition control. Detailed and proper insight into ALD reactions mechanisms provides an avenue towards knowledge-based improvement of ALD processes and therefore towards a higher degree of control and improved ALD materials. *In situ* and *operando* characterisation, carried out during thin film deposition, can contribute greatly to the development of such a proper understanding of ALD reaction mechanisms [5-7]. One such *in situ* and *operando* characterisation method is ambient pressure x-ray photoelectron spectroscopy (APXPS), which we have used, together with density functional theory (DFT), to study the ALD of HfO_2 on a SiO_2 surface from tetrakis(dimethylamido) hafnium (TDMAHf) and water.

The APXPS and DFT results provide clear evidence for a bimolecular surface reaction mechanism in the initial half-cycle of ALD. This bimolecular mechanism proceeds via a β-hydride elimination reaction between two neighbouring, surface-adsorbed TDMAHf complexes. Without this intermolecular interaction any conceivable surface chemical reaction mechanism is so endothermic that it does not proceed under standard reaction conditions. Surface hydroxyls are found not to play any role in the initial surface chemistry of the TDMAHf ALD on SiO_2; indeed, our results provide a straightforward explanation of why the process is possible on hydroxyl-free surfaces, even though standard ligand exchange reaction models of transition metal amido complex ALD require the presence of surface hydroxyls. The APXPS and DFT results provide detailed insight also into the chemistry of subsequent half-cycles.

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TF-Contributed On Demand-88 Feature Scale Model to Investigate Aspect Ratio Dependency of Si_xN_y Atomic Layer Deposition using Si_2Cl_6 and NH_3*,* ***Evrim Solmaz,*** University of Texas at Austin*; S. Ryu, J. Uh,* Samsung Electronics, Korea (Republic of)*; L. Raja,* University of Texas at Austin

Semiconductor memory fabrication applications rely on deposition of very thin silicon nitride films with uniform film thickness and electrical properties. Such high quality film requirements and miniaturization has made atomic level control a necessity, which can be achieved via atomic layer deposition (ALD) with a low thermal budget. While ALD has been studied experimentally by many authors, there exist significant gaps between recent experimental observations and the general understanding of the practical implications of the ALD process. In this work, a computational model of thin film deposition for silicon-based ALD applications is developed. The model provides a surface chemistry mechanism for the deposition of hexachlorodisilane (Si_2Cl_6) on a silicon wafer. The mechanism informs us on the sticking probability of the Si_2Cl_6 precursor on a Si surface as well as a consequential active surface reaction site instability. This reaction chemistry is applied to simulate ALD in deep-hole structures of a wafer using a particle kinetic model. This feature scale model was able to demonstrate aspect ratio dependent deposition (ARDD), a phenomenon characterized by neutral shadowing and Knudsen transport effects. The statistical nature of the deposition dynamics in features with a small critical dimension of ~100 nm and high-aspect ratios is also predicted. The model demonstrates an increase in deposition completion time as aspect ratio increases, while emphasizing deposition surface area enlargement as an important factor.

TF-Contributed On Demand-91 Nucleation and Growth of Thermal ALD Au Films - Towards Coalescence of Ultrathin Films*,* ***Benjamin Greenberg,*** *J. Avila, J. Woodward, N. Nepal, B. Feigelson, V. Wheeler,* U.S. Naval Research Laboratory

Gold is the metal of choice in many electronic and optoelectronic applications due the beneficial combination of high electrical and thermal conductivity with excellent resistance to corrosion. For this reason, significant efforts have been made to develop ALD Au precursors, resulting in two possible options - $Me_3Au(PMe_3)$ and $Me_2Au(S_2CNEt_2)^{1,2}$. The latter is particularly interesting due to its ability to thermally deposit films with near bulk resistivities[2]. In this case, fully coalesced films required relatively thick (>20nm) films and thus limits their use as transparent metal films in applications such as neutral beam splitters, transparent electrodes, and thermal insulating and solar control coatings. In this work, we focus on understanding the nucleation and growth mechanisms of thermal ALD Au films and the influence of substrate and deposition parameters on the ability to reduce the thickness at which fully coalesced films can be attained.

ALD Au films were deposited sing $Me_2Au(S_2CNEt_2)$ and ozone at temperatures (T_g) from 125-200°C. The Au precursor was held at 110°C and delivered using a vapor boosted process. Initial films were deposited on a variety of substrates with different chemical inertness, wettability, and roughness including sapphire, Si, ALD TiN, Au, and others. SEM images reveal that growth on all substrates proceeds similar to other CVD Au processes with nucleation and growth of individual islands, which then form elongated structures that lead to percolation and eventually fully coalesced films. This type of growth makes it difficult to define thickness with traditional methods such as ellipsometry. Thus, we use a combination of XRR, ellipsometry, and XPS to evaluate the films and define ALD windows. For instance, at 200 cycles, film thickness is constant at ~24 nm from 150-200°C but the density and total coverage increases with T_g.

Initial results at 150°C show that the percolation threshold (t_c) is dependent on substrate with t_c on Au < sapphire < Si < ALD TiN, suggesting that thinner films can be obtained on more inert surfaces. Thick films (50-60nm) show resistivities of 3-4.8 μΩ cm depending on substrate and pinhole density. At low T_g here, the kinetic freezing model can be used to describe the crossover from island growth to coalescence[3]. This suggests that t_c is influenced by growth temperature, surface diffusion constant, and surface energy. We will discuss our approach to decouple these aspects and their resulting effect on reducing t_c.

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TF-Contributed On Demand-94 Modification of Mesoporous Thin Films by Atomic Layer Deposition for the Fabrications of Electrocatalysts for Oxygen Evolution Reaction*, M. Raza,* Humboldt University Berlin, Germany*; M. Frish, R. Kraehnert,* Technical University of Berlin, Germany*;* ***Nicola Pinna,*** Humboldt University Berlin, Germany

The principal aim of this study is to improve the electrochemical water splitting efficiency by developing novel electrodes along with a significantly lower contents of catalytically active species to curtail the cost of the catalysts as a major challenge. Herein, novel catalysts are synthesized by depositing catalyst layers directly onto mesoporous thin films as conductive supports providing a reasonably large surface area to the system. Active catalyst materials such as IrO_x and NiO are deposited by atomic layer deposition using different low and high vapour pressure metal precursors. The composition, morphology and crystallinity of the deposited film is controlled by varying different deposition parameters. Varying amount, size and morphologyof the metal oxides catalysts were homogeneously deposited onto a series of mesoporous films consisting of transition metal oxides. The structural, morphological and the electrocatalytic oxygen evolution reaction of the NiO (in basic media) and IrOx (in acidic media) loaded heterostructures were thoroughly investigated in order to derive clear structure-property relationship.

TF-Contributed On Demand-97 Optimization of 1D Core-Shell Heterostructures for Gas Sensing*, **Nicola Pinna**, M. Raza,* Humboldt University Berlin, Germany

Hierarchical core-shell heterostructures composed of p-, n-type and insulating metal oxide shells deposited onto carbon nanotubes (CNTs) were synthesized using atomic layer deposition. Precisely controlled films of alternating metal oxides were uniformly deposited onto the inner and outer walls of the CNTs. The morphological, microstructural and electrical characteristics of the as prepared core-shell heterostructures were thoroughly investigated. The electrical resistance measurements highlighted the large influence of the metal oxides thickness and charge carriers types on increasing of many order of magnitude the baseline resistance of the core-shell heterostructures with various thicknesses of the metal oxide shell layers, suggesting that the conductivity of the sensors is dominated by Schottky barrier junctions across the n-p interfaces.

The behavior of our sensors was investigated for low concentrations of volatile organic compounds and pollutants. The gas sensing response of the heterostructures showed a strong dependence on the thickness of the metal oxide shell layers and the type of heterostructures formed. On the basis of the morphological, microstructural and electrical characterization and sensing results, the sensing mechanism which accounts for the marked variation in the resistance during the interaction of the target gas molecules will be discussed.

TF-Contributed On Demand-100 ALD-based Nanolayers for Germanium Surface Passivation*, **Willem-Jan Berghuis**, R. Theeuwes, B. Macco, E. Kessels,* Eindhoven University of Technology, Netherlands

The passivation of Ge and SiGe surfaces by ALD films has been a long-standing challenge. Currently this challenge has become extra relevant due to the application of (Si)Ge as channel materials for the newest gate-all-around field-effect transistors[1], but also regarding the interest in Ge and SiGe as light emitting media for silicon photonics[2]. These emerging applications put different demands on the materials, thicknesses and process conditions that can be used to provide the required level of surface passivation to enable satisfying device performance. It is therefore relevant to develop an extensive toolbox of passivation materials and techniques to meet these demands.

In this work we discuss our latest findings about several potential passivation schemes for Ge including atomic layer deposited Al_2O_3 as well plasma enhanced chemical vapor deposited (PECVD) a-Si:H and PO_x in stacks such as PO_x/Al_2O_3 and a-Si:H/Al_2O_3. We have determined the surface recombination velocity (S_{eff}), fixed charge density (Q_f), and in some cases also the interface defect density (D_{it}) and an estimation of the capture cross-sections of electrons and holes. With these parameters we were able to determine the passivation potential of each of these schemes and the type of application for which they are suited best. Moreover, we have visualized several of the investigated interfaces by cross-sectional TEM and we have linked our findings on Ge to earlier findings on Si surfaces. Key achievements of our work include a surface recombination velocity on Ge as low as 2.7 cm/s and a negative fixed charge density as high as (8-15)x10^{12} cm^{-2}.

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TF-Contributed On Demand-103 The Effect Growth Conditions on the Phase Composition and Microstructure of Gallium Oxide Thin Films Deposited Using MOCVD*, J. Tang, **Kunyao Jiang**, A. Park, L. Gu, R. Davis, L. Porter,* Carnegie Mellon University, USA

Over the past decade Ga_2O_3 has accrued increased interest because of its ultra-wide bandgap, its availability as single-crystal substrates, its high electric breakdown field, and its excellent Baliga's figure of merit (BFOM) for power electronics. Ga_2O_3 possesses four different verified polymorphs: the rhombohedral (α), monoclinic (β), orthorhombic ε(k), and defective spinel (γ) phases. The majority of research has been conducted on β-Ga_2O_3, because it is the thermodynamically stable phase and the phase produced in melt-grown substrates. However, this phase possesses significant anisotropic physical and electrical properties. The other polymorphs (in epitaxial form) are of interest, as their crystal structures have higher symmetry, and all have wide bandgaps (~4.7–5.3 eV) and high transparency in the visible and UV regions. In particular, ε(κ)-Ga_2O_3 is ferroelectric with a high spontaneous polarization that could be exploited in heterostructures for high electron mobility transistors. In this study, we investigated the effects of selected growth conditions on the heteroepitaxial growth of β- and ε-Ga_2O_3 films on 0.15° off-axis (toward m-plane), (0001) sapphire substrates using low-pressure metal-organic chemical vapor deposition (MOCVD). TEGa and high purity O_2 were used as precursors and N_2 was used as both the carrier gas for TEGa and the diluent gas. The vent-to-run mode was applied for the growth to stabilize the flow rates of both precursors before entering into the reaction chamber. During the growth, the chamber pressure was kept at 20 Torr. The flow rate of TEGa ranged from 0.30 to 1.92 sccm, while the flow rate of O_2 was kept as 500 sccm and the temperature was varied between 515℃ to 570℃. XRD 2θ-ω results showed that deposition of the ε-phase is achieved at the lower growth temperatures and higher TEGa flow rate (low VI/III ratio) whereas the β-phase forms at higher growth temperature and lower TEGa flow rate (high VI/III ratio), with mixed-phase growth for conditions in between. The out-of-plane epitaxial relationships are (-201)β-Ga_2O_3 || (0001) α-Al_2O_3 and (0001)ε-Ga_2O_3 || (0001)α-Al_2O_3. In addition, the microstructure of the films showed a dependence on the phase composition. Using the growth conditions for the films with the mixed phases tended to result in rough and discontinuous films. XRD phi (ϕ) scans were conducted to characterize the in-plane microstructure. The results suggest that the ε-Ga_2O_3 films have a dominant in-plane orientation. In this presentation we will discuss the MOCVD growth conditions that lead to nominally phase-pure β- and ε-Ga_2O_3 films and the metrics associated with achieving an optimized microstructure.

TF-Contributed On Demand-106 Temporal Evolution of Electrical Contact Resistance Observed via Improved Conductive Atomic Force Microscopy*, **Saima Sumaiya**, M. Baykara, M. Vazirisereshk, R. Chen, A. Martini,* University of California Merced

Electrical contact resistance (ECR) is a crucial parameter to optimize the design and, evaluate the contact reliability and performance of small-scale electrical and electro-mechanical systems. Even though there have been extensive studies of ECR at macro- and microscopic length scales, the fundamental mechanisms affecting ECR on the nanoscale need further investigation. Although conductive atomic force microscopy (C-AFM) appears to be an ideal method to measure nanoscale ECR, related measurements suffer from a high degree of variability and poor reproducibility due to a number of factors including variations in sample roughness, changes in humidity, adsorption of contaminants, temperature fluctuations as well as deformation of the tip apex. Here, we explore the temporal evolution of ECR at nanoscale contacts via an improved C-AFM technique that circumvents the adverse effects of the aforementioned factors [1]. Experimental results, complemented with molecular dynamics (MD) simulations, show that ECR decreases with time due to local pressure activated contact aging i.e. an increase in real contact area due to atoms diffusing into contact [2]. We additionally observe spontaneous jumps in ECR during measurements performed over several minutes, which are suppressed through the application of higher normal loads.

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TF-Contributed On Demand-109 Advances in Plasma-Enhanced Atomic Layer Deposition of Ga_2O_3 and $(Al_xGa_{1-x})_2O_3$ Films*, **Virginia Wheeler**, N. Nepal, S. Qadri, J. Avila, B. Downey, V. Gokhale, A. Lang, R. Stroud, D. Meyer,* Naval Research Laboratory

Ga_2O_3 is a promising ultra-wide bandgap material for future power electronics. While β-Ga_2O_3 is the most stable and studied of six Ga_2O_3 polymorphs, the slightly less energetically favorable α-, ε-, and κ-Ga_2O_3 phases have unique characteristics that can be exploited such as larger bandgaps, alloying for dopant control, or polarization beneficial to the formation of two-dimensional electron gas (2DEG) channels. Recently, delta-doping and heterojunctions with $(Al_xGa_{1-x})_2O_3$ have emerged as critical aspects to realizing devices based on Ga_2O_3, both of which can be addressed by thin plasma-enhanced atomic layer deposition (PEALD) layers. PEALD is a conformal, energy-enhanced synthesis method for thin films due to its many advantages compared to thermal processes, including: deposition at reduced growth temperatures, access to metastable phases, improved crystallinity, and increased growth rates. Previously, we have demonstrated the ability to control Ga_2O_3 phase using PEALD [1,2]. Here, we use PEALD to produce high-quality heteroepitaxial Ga_2O_3 and $(Al_xGa_{1-x})_2O_3$ (AlGO) films and investigate materials properties such as doping, ternary solubility limits and electrical performance.

All Ga_2O_3 and AlGO films were deposited in a Veeco Fiji G2 reactor equipped with a load lock and turbo pump using trimethygallium, trimethylaluminum, and O_2 plasma at 295-400°C. While PEALD is beneficial for depositing thin films of metastable phases, practical devices often require much thicker barrier and active layers. Thus, we investigated integrating PEALD metastable Ga_2O_3 films with traditional semiconductor deposition techniques, like molecular beam epitaxy (MBE), capable of extending these layers beyond 100 nm. The same MBE conditions were used to deposit Ga_2O_3 films on GaN substrates with and without PEALD ε(κ)-Ga_2O_3 nucleation layers. Those without the PEALD metastable nucleation layer resulted in stable β-phase films, while those with nucleation layers resulted in pure ε(κ)-phase films. This shows the importance of PEALD for realizing practical device structures using metastable phases.

Finally, to investigate heterojunctions for 2DEG formation, $Al_xGa_{1-x}O$ films were developed. While the full stoichiometric range could be reached using a PEALD digital alloying method, crystallinity was lost above x = 0.2 for the β phase, x = 0.35 for the ε(κ) phase, and x=0.6 for the α phase. Initial device structures will be shown in order to establish the feasibility of these films in device applications.

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[2]Boris,et al. *JVSTA* 2019, 37(6), 060909

TF-Contributed On Demand-112 Structure Related Investigations and Fracture Resistance of Ti-Mo-B Thin Films*, **Christoph Fuger**, A. Hirle, R. Hahn,* CDL-SEC, TU Wien, Austria*; M. Weiss,* Institute of Chemical Technologies and Analytics, TU Wien, Austria*; O. Hunold,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; P. Polcik,* Plansee Composite Materials GmbH, Germany*; H. Riedl,* CDL-SEC, TU Wien, Austria

Transition metal diborides (TMB_2) offer a great potential for being applied as protective coatings on various components in industrial applications, especially for high-performance components, i.e. turbine blades. Due to very promising material characteristics, arising from the hexagonal crystal structure with an alternating stacking of covalent bonded boron hexagons and metal planes (AlB_2 prototype, SG191, α), TMB_2 based coating materials experience increasing attention. Density functional theory (DFT) calculations of various TMB_2 allowed a classification by its elastic properties (bulk modulus, shear modulus, Poisson's ratio), into brittle and ductile regions. The results suggest that combining brittle but hard TiB_2 ($G/B > 1.0$, $\nu < 0.15$) with ductile MoB_2 ($G/B < 0.55$, $\nu > 0.26$) could have a great potential for a material system with enhanced fracture resistance, while sustaining high hardness.

Therefore, we deposited TiB_2 and Ti-Mo-B based coatings by DC magnetron sputtering using TiB_2/C 99/1, TiB_2/MoB 95/5 mol%, TiB_2/MoB 90/10 mol%, as well as TiB_2/MoB 80/20 mol% powder metallurgical produced 6-inch targets. For the synthesis we applied an industrial scale as well as an in-house developed deposition system. Structural analysis and mechanical properties showed that this material system is highly sensitive regarding the plasma distribution and stoichiometry of the thin films. The chemical composition of all coatings has been analyzed by liquid inductively coupled plasma optical emission spectroscopy (ICP-OES) revealing decreasing boron content with increasing Mo. Furthermore, micromechanical cantilever bending experiments have been applied for determining the materials critical stress intensity factor (K_{IC}). Moreover, the oxidation behavior and thermomechanical properties have been investigated to gain a broader insight into the Ti-Mo-B based material system.

Keywords: Transition Metal Diborides, Fracture Resistance, Mechanical Properties, Oxidation Resistance, Physical Vapor Deposition

TF-Contributed On Demand-115 2D Mos_2 Layers Synthesized by ALD as Diffusion Barriers in Interconnects*, **Sanne Deijkers**, A. de Jong,* Eindhoven University of Technology, Netherlands*; H. Sprey, J. Maes,* ASM, Belgium*; E. Kessels, A. Bol, A. Mackus,* Eindhoven University of Technology, Netherlands

The deposition of closed nanometer-thick films as required for the further miniaturization of nanoelectronics is a real challenge. Conventional TaN/Ta barriers in Cu interconnects fail at thicknesses below 3 nm [1] and cannot be scaled further. To reduce the thickness of the barrier, the TaN/Ta layers could be replaced by atomically-thin 2D materials, such as 2D transition metal dichalcogenides (TMDs). In this work we report on the diffusion barrier performance of MoS_2 synthesized by atomic layer deposition (ALD). Up to this point, research concerning 2D TDMs as barrier layers involved chemical vapor deposition (CVD) processes [2]. ALD provides the control and high conformality that is required to deposit closed ultra-thin films.

MoS_2 layers have been deposited using a plasma-assisted ALD process using $Mo(NMe_2)_2(N^tBu)_2$ as the precursor and H_2S plasma as the co-reactant. The barrier performance of the MoS_2 layers against Cu diffusion is characterized by time-dependent dielectric breakdown (TDDB) tests. MoS_2 layers of 4 nm (processed at 450°C) show a mean time to failure ($TTF_{50\%}$) of 8.4 h (30 077 s), where the longest observed breakdown time is72 hours. Also, MoS_2 layers of 6 nm result in a substantial improvement in performance as compared to barrierless structures ($TTF_{50\%}$=187s).

Depositions have been performed at various temperatures (200, 350 and 450°C) to study the influence of the morphology on the barrier performance and to obtain insight in the Cu diffusion mechanism through the barrier layer. From previous studies it is known that the MoS_2 growth evolves from amorphous to crystalline 2D layers with increasing deposition temperature, and eventually to out-of-plane-oriented (OoPO) films [3]. The first results show that the crystalline OoPO MoS_2 films deposited at 450°C display good barrier performance.

Continued optimization of the thin MoS_2 layers can result in further improvement in the barrier performance. In the presentation the influence of the morphology of the MoS_2 layers on the barrier performance will be discussed.

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TF-Contributed On Demand-118 Polarization Sensitive Characterization of 2D Metasurfaces Fabricated by Direct Laser Writing*, **Micheal McLamb**,* University of North Carolina at Charlotte*; Y. Li,* University of Chicago*; P. Stinson, S. Park, G. Boreman, T. Hofmann,* University of North Carolina at Charlotte

Fabrication of 2D metasurfaces is often time consuming and expensive involving complex lithographic processes. One of the most intricate parts of state-of-the-art fabrication of metasurfaces is the design and construction of the lithographic mask. Therefore, maskless direct laser writing-based techniques are currently being investigated as a suitable alternative, providing cost-effective, rapid prototyping of 2D metasurfaces. Here we report on the fabrication and polarization sensitive infrared-optical characterization of 2D metasurfaces composed of rectangular Au bars. The investigated 2D metasurfaces were fabricated using a three-step process which will be discussed in detail in our presentation. First, a sacrificial layer was deposited using a two-photon polymerization process, which allows maskless fabrication of the inverse 2D metasurface. This step is followed by metallization and subsequent sacrificial layer lift off. As a result, a 2D metasurface with high fidelity is obtained. The infrared reflection measurements of the fabricated 2D metasurfaces were carried out in the range from 3 µm – 16 µm and reveal several resonances which can be distinguished by their response to the varying input polarization. The observed infrared reflectivity is found to be in good agreement with finite element calculations. Based on the infrared-optical response of the fabricated 2D metasurfaces, we conclude that two-photon polymerization allows for simple and maskless fabrication of 3D metasurfaces designed for the infrared spectral range.

TF-Contributed On Demand-121 Reciprocal Plasmonic Metasurfaces for the Detection of Ambient Changes Induced by Atomic Layer Deposition*, **Micheal McLamb**,* University of North Carolina at Charlotte*; Y. Li,* University of Chicago*; P. Stinson, S. Park,* University of North Carolina at Charlotte*; J. Lentz,* Air Force Research Laboratory*; T. Hofmann,* University of North Carolina at Charlotte

Plasmonic metamaterials exhibit strong localization and enhancement of fields at selective frequencies that shift substantially when introduced to analytes. This has led to interest in using plasmonic metamaterials as improved devices for sensing applications. We have recently discovered that reciprocal metasurfaces composed of two metasurfaces separated by dielectric spacer fins exhibit a very strong sensitivity to ambient changes using finite element model calculations. The reciprocal plasmonic metasurface was additively manufactured via two-photon lithography with a negative tone photoresist followed by electron beam deposition of Au. Incremental conformal coatings of amorphous Al_2O_3 were deposited using atomic layer deposition with the optical response monitored between depositions using FTIR microscopy to assess device sensitivity to small changes in ambient environment. The main absorption feature displays a gradual red shift per iteration of amorphous Al_2O_3 coating confirming that reciprocal plasmonic metasurfaces are suitable for sensing applications.

TF-Contributed On Demand-124 Effect of Film Composition and Structure on the Photocatalytic Activity of Metal Oxide Atomic Layer Deposition Thin Films, ***Halil Akyildiz**, S. Islam, S. Ozkan,* Bursa Uludag University, Turkey

Thin film photocatalysis is a promising approach for the elimination of organic pollutants using solar energy. Immobilized catalyst films can be used multiple times without being lost in the medium of the reaction (i.e. usually a liquid solution). Atomic layer deposition being capable of forming conformal and uniform films on high aspect ratio substrates enables immobilization of the catalyst material while maintaining the high surface area needed for faster reactions. Textile fabrics, as inexpensive high surface area substrates, are deposited with thin films of various compositions of TiO_2, ZnO, and Al_2O_3 materials. Coated fabric samples were investigated in terms of their photocatalytic activity for the degradation of organic dyes such as methylene blue, as a model system. The structure of the film materials plays a significant role in the photocatalytic performance as well as the composition. Since the repeatable photocatalytic use of the films is one of the reasons for the immobilization, the same sample was tested for photocatalytic activity against a methylene blue model solution several times. Results showed that immobilized films show photocatalytic activity each time with a slight reduction in the performance both in terms of reaction time and reaction saturation. Furthermore, in this study photocatalytic activity of these samples was tested in actual textile effluents by measuring the chemical oxygen demand (COD) changes of the solutions. This way a long-proposed use of the films is tested in an actual environmental cleaning situation where multiple organic pollutants were present at various pH values. Films are characterized with UV-Vis, XRD, XPS, and PL spectroscopy techniques as well as electron microscopy in order to explain the observed photocatalytic activity of the different compositions of the films.

TF-Contributed On Demand-127 Effect of Heat and Plasma Treatment on Carborane Self-Assembled Monolayers (SAMs) on Copper, ***Rupak Thapa**, L. Dorsett, S. Malik, R. Bale, S. Wagner, D. Bailey, A. Caruso,* University of Missouri-Kansas City*; J. Bielefeld, S. King,* Intel Corporation*; M. Paquette,* University of Missouri-Kansas City

Self-assembled monolayers (SAMs) have important applications in surface engineering and thin-film processing. Their uses include chemical sensing, area-selective deposition, and modification of various surface properties such as wetting, adhesion, and friction/lubrication. In this study, we have investigated the modification of copper surfaces by thiol-carborane SAMs. Carboranes have been used to deposit boron carbide films using plasma-enhanced chemical vapor deposition for low-k interlayer dielectrics, neutron detection, and a variety of protective coatings. These are symmetric twelve-vertex molecules possessing labile hydrogen atoms at each vertex capable of crosslinking under the influence of heat or plasma. Carborane precursors are unique among other organic precursors due to their reactivity and volatility that allow vapor-phase deposition and 3D growth with potentially fewer defects. It has been shown that carborane-based SAMs provide corrosion resistance on silver and copper and have the ability to modify the electronic properties (e.g., work function) of gold, silver, and germanium. Despite different applications, the behavior of these SAMs under more aggressive conditions (e.g., high temperature, high humidity, plasma exposure) is not well documented. The thermal stability of SAMs is relevant for certain applications themselves (e.g., molecular electronics, protective coatings) as well as in assessing their suitability for further processing with high-temperature steps. In addition, it is important to study the effect of plasma on SAMs since plasma treatment can be used as an intermediary step as a way to either functionalize, stabilize or remove films. Here, we investigate the influence of heat and plasma on carborane SAMs on copper using in situ ellipsometry, in situ X-ray photoelectron spectroscopy, and water contact angle measurements. We heat the SAMs to various temperatures (150—400 °C) to investigate their thermal stability. We also use various plasmas (N_2, O_2, H_2, Ar) to determine how these stabilize, degrade and/or otherwise modify the SAMs. We show that both thiol-carborane SAMs on copper demonstrate significant thermal stability up to 400 °C, and the results suggest that SAMs based on 1,2-dithiol-*o*-carborane containing two thiol groups are more thermally stable than those based on 9-thiol-*m*-carborane containing one. The results from the plasma treatment study demonstrate multiple effects such as parasitic film growth, surface saturation, oxidation, and other functionalization depending on the gas used. We found that 1,2-dithiol-*o*-carborane SAMs appear to show more significant parasitic growth and/or more rapid saturation than do 9-thiol-*m*-carborane SAMs. In general, we found that all types of plasma treatments oxidize the SAMs, although to different extents. The oxidation of SAMs based on 1,2-dithiol-*o*-carborane is slower than in the case of those based on 9-thiol-*m*-carborane.

TF-Contributed On Demand-130 Challenges in the Fabrication of Good Quality Bismuth Ferrite Films by Chemical Vapor Deposition, ***Mahendra Acharya**, C. Joshi,* University of Alabama*; T. Gosavi, U. Alaan, J. Plombon,* Intel Corporation*; A. Gupta,* University of Alabama

Bismuth ferrite ($BiFeO_3$, BFO), a widely explored room-temperature multiferroic material, is a prospective candidate for application in logic and memory devices. A robust coupling between magnetism and ferroelectricity in it gives rise to an interesting property of magnetoelectricity. Magnetoelectricity leads to the possibility of low energy switching of magnetic field using an electric field that makes BFO a potential component for more energy-efficient and scalable device architecture.

After the pioneering work of Prof R. Ramesh in 2005, nearly a dozen of work has been published on the synthesis of BFO films by CVD. No good-quality saturated ferroelectric hysteresis loop (at room temperature) has been reported in the latter works. We wanted to explore the challenges in the synthesis of BFO with a good ferroelectric property by CVD technique and figure out ways to overcome the challenges by a systematic study of the effect of process parameters and stoichiometry on the ferroelectric property of the material.

In this work, good quality smooth epitaxial BFO films varying in thickness from 20 nm to 1000 nm are deposited at 600 °C using direct liquid injection equipped metalorganic CVD on lattice-matched $SrTiO_3$ (STO) and $SrRuO_3$ (SRO) buffered STO substrates with RMS roughness <1nm and <3 nm respectively. Films were deposited using triphenyl bismuth(III) and Fe(III) acetylacetonate as metalorganic precursors over a range of composition, temperature, and pressure. Ferroelectric and leakage characteristics of BFO are found to be greatly dependent on the stoichiometry of the films. Saturated ferroelectric loops (at room temperature) were obtained when the films are slightly Bi-rich (4-5%), Fe-rich films tend to give open hysteresis loop (even though they have a lower leakage current). Films deposited above or below an optimum pressure value (4 Torr in our setup) did not furnish good ferroelectric loops. Good quality films have been deposited at higher temperatures 650 and 675 °C, the effect of deposition temperature on the ferroelectric property is currently being studied.

TF-Contributed On Demand-133 Study and evaluation of a $MASnI_3$ Perovskite/CZTS solar cell using Numerical Simulation (SCAPS-1D), ***Ana Cecilia Piñon Reyes**,* BUAP, Mexico

Actually, perovskite based solar cells with ABX_3 as a generic structure, have reached efficiencies about 25.5% (National Renewable Energy Laboratory-NREL). Among the main structures, we have hybrid solar cells based on the organo-metallic halide $CH_3NH_3PbI_3$, however, due to their lead content, they have turned out to be toxic and harmful to health, for this reason other alternatives have been sought. This is the main reason to propose a $MASnI_3$ perovskite in our research.

There are different depositing techniques for $MASnI_3$ material, the most widely used are vacuum thermal evaporation, electrodeposition and spin coating but the characteristics will vary according to experience, quality of reagents, laboratory infrastructure, etc. However, the behavior and optimal parameters of the perovskite solar cells can be demonstrated by means of simulations with SCAPS-1D. Spiro-OMeTAD is usually used as HTL, but we replaced it with a kesterite (CZTS) layer; this provides us the advantage of having two absorbent materials that have similar band gaps 1.3 eV for $MASnI_3$ and 1.4 eV for CZTS, as a consequence they showed an excellent affinity in their interface. Our proposed tandem solar cell is made up of the following layers: SnO_2:F (FTO)/TiO_2 (ETL)/$MASnI_3$/CZTS (HTL)/Au.

The analysis carried out shows that the photovoltaic parameters J_{sc}, V_{oc}, FF and PCE are strongly influenced by the thickness of the absorbent layer. The thickness was varied from 250 to 1000 nm to obtain the optimal value. Simulations showed that J_{sc} increases abruptly up to 500 nm and then it varies slowly with the thickness. The best J_{sc} obtained value was 31.74 mA/cm^2 with a thickness of 700 nm; this was mainly attributed to the large absorption coefficient. The V_{oc} shows a significant decrease, which can be attributed to the improved recombination of the free charge carriers in the thicker absorbent.

Furthermore, the highest PCE is 20% when we used a 500 nm perovskite layer, and it decreases with a further increase in the thickness of the absorbent layer. This could be due to the thickness of the absorbent layer is thinner than the diffusion length of the charge carriers; therefore, most of the charge carriers reach the electrodes and thereby increase the PCE.Besides, recombination occurs in a thick absorbent layer and therefore PCE decreases with a further increase in thickness. The decrease on defect density N_t of the absorbent layer increases the PCE, FF, V_{oc} and J_{sc} of the solar cell; 10^{14} cm^{-3} was taken as the best value. The final optimized parameters of our solar cell were 500 nm and 300 nm on thickness for $MASnI_3$/CZTS layers respectively to obtain PCE 20%, FF 67%, J_{sc} 31.31mA/cm^2 and V_{oc} 960 mV.

Keywords: Perovskite, kesterite, CZTS, tandem solar cell, SCAPS 1D

TF-Contributed On Demand-136 Analysis and Testing of Nanocrystalline Diamond Thin Film Failure During H- Stripping*, Leo Saturday,* University of Tennessee Knoxville*; L. Wilson, C. Luck, J. Fowlkes,* Oak Ridge National Laboratory*; P. Rack,* University of Tennessee Knoxville*; N. Evans,* Oak Ridge National Laboratory

Nanocrystalline diamond (NCD) films are used at accelerator beamlines as electron stripper foils for their ideal thermal and mechanical robustness, as well as the minimal scattering carbon has on the interacting beam. While the thermal and mechanical stability of NCD allow for its prolonged use in many beamlines, there are concerns of foil failure in high energy beamlines such as the Spallation Neutron Source (SNS) where beam induced heating is expected to bring the material near the sublimation temperature. In this work, NCD stripper foils are tested using an electron beam capable of simulating the heat load of the SNS H- ion beam to elucidate potential failure mechanisms. In situ and postmortem diagnostics are used to identify changes to the foil and how they relate to electron stripper foil failure. These diagnostics along with COMSOL simulation allow us to equate the test stand current density to the SNS beamline and predict foil failure conditions. Sublimation of the NCD foil is of particular interest as it has been indirectly examined previously in the SNS beamline. As such, NCD foil sublimation due to interacting beam is explicitly examined in this work.

TF-Contributed On Demand-139 Surface Functionalization of Nanoporous Carbon Fibers by Vapor Phase Methods for CO_2 Capture*, Stephan Prünte,* *G. van Straaten,* Eindhoven University of Technology, Netherlands*; D. van Eyck, O. Diaz-Morales, J. van Dijck, H. de Neve,* Carbyon, Netherlands*; M. Creatore,* Eindhoven University of Technology, Netherlands

The removal of excess CO_2 from the atmosphere is expected to play a major role in the mitigation of global warming. While CO_2 sequestration at fossil fuel power plants mostly employs wet chemical routes, CO_2 sequestration from ambient air is much more challenging and there is an urgent need for high-performance sorbents. Solid-state adsorbents, consisting of CO_2-binding moieties on porous supports, can deliver high CO_2 capture capacities with low energy requirements.

In this contribution we report on the functionalization of porous carbon fibers by self-limiting vapor-phase techniques. Functionalization occurs either via i) ALD of Al_2O_3 based on trimethylaluminum and H_2O, ii) exposure to a cyclic azasilane molecule (2,2-dimethoxy-1,6-diaza-2-silacyclooctane) to introduce amine functionalities or iii) ALD Al_2O_3 followed by exposure to the azasilane molecule. Given the high specific surface area of the carbon fibers, which exceeds 1000 m^2/g with a pore size in the range of 0.5-1.2 nm, the above-mentioned precursors were dosed in multi-pulses to deliver conformal functionalization of the sample.

The self-limiting nature of the two processes was verified by weight gain measurements. The increase in weight relative to the pristine samples saturated at 11% for Al_2O_3 and 23% for amine functionalization, respectively. For case iii), the relative weight gain upon azasilane exposure saturated at 3.1%. XPS analysis confirmed successful Al_2O_3 and amine functionalization in all cases. SEM/EDX measurements of the distribution of Al and Si over the fiber cross-section revealed a homogenous modification of the fibers.

Preliminary investigations of CO_2 adsorption capacities were performed by adsorption from humidified synthetic air followed by heating in an N_2 stream, with desorption monitored by mass spectrometry. The largest CO_2 capture capacities (0.18 mol per kg) were observed for the amine functionalized sample. This sample was able to store 0.2 mol CO_2 per mol amine, similar to amine-based CO_2 sorbents on silica supports earlier reported in literature[1]. Double functionalization, instead, lead to a somewhat lower overall capacity (0.12 mol per kg) but far superior kinetics, indicating that this approach might be valuable for compact, high-throughput CO_2 capture systems.

The presented research demonstrates the potential of modifying porous carbon fibers by grafting CO_2 adsorption functionalities on their internal surface. Future engineering of porous materials by self-limiting vapor-phase functionalization and tuning their gas sorption kinetics may pave the way towards realizing efficient direct air capture.

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TF-Contributed On Demand-142 Redox-Active Polymer Thin Films by MLD for Enhanced Electrochemical Desalination*, Matthias Young,* *Q. Wyatt, R. Gettler, N. Paranamana, T. White, X. He,* University of Missouri-Columbia

Capacitive deionization (CDI) is an emerging technology which shows promise for improved energy efficiency for desalination over reverse osmosis (RO). New CDI electrode material concepts aimed at increasing the specific capacitance of the electrodes and reducing diffusion losses promise to lower cost and reduce energy consumption for desalination and increase the efficiency of CDI. Supercapacitive conjugated amine polymers (CAPs), such as polypyrrole and polyaniline, are promising candidates for CDI electrode coatings which exhibit both high ion binding capacities (> 500 F/g) and high electrical conductivity (>500 S/cm). Unfortunately, conventional CAP deposition techniques, such as oxidative polymerization and electrodeposition, produce non-uniform CAP films with minimal control over film molecular structure and thickness. Here, we demonstrate the deposition of thin films of CAPs uniformly onto electrode surfaces using molecular layer deposition (MLD), and study the impact of the MLD deposition process conditions on the structure and properties of the CAP films. Specifically, we evaluate the effect of film thickness and local polymer structure on the ion uptake capacity and rate, and discuss these results in light of insights into the CAP MLD growth mechanisms. The results we report demonstrate MLD as a platform for synthesizing thin films of CAPs, which can be used to enable high efficiency desalination.

TF-Contributed On Demand-145 Smoothing Surface Roughness Using Al_2O_3 Atomic Layer Deposition*, T. Myers,* University of Colorado Boulder*; J. Throckmorton, T. Hatwar, R. Borrelli, M. O'Sullivan,* L3Harris Space & Airborne Systems*;* ***Steven George,*** University of Colorado Boulder

Al_2O_3 atomic layer deposition (ALD) was used to smooth the roughness on silicon wafers. The initial silicon wafers were obtained prior to chemical mechanical polishing (CMP). These silicon wafers had an average RMS surface roughness of 3.3 nm as determined by atomic force microscopy (AFM) measurements. AFM line scans also measured an average lateral spacing of ~400 nm between the surface asperities. After 3000 Al_2O_3 ALD cycles, the RMS roughness of the wafers was reduced to 1.5 nm. Likewise, the average lateral spacing between the surface asperities increased to ~900 nm. The RMS roughness decreased and the average lateral spacing increased progressively with number of Al_2O_3 ALD cycles. Additional Al_2O_3 ALD cycles beyond 3000 cycles produced little change in the RMS roughness or average lateral spacing. The smoothing ability of the Al_2O_3 ALD starts to limit when the lateral distance between the surface asperities is much larger than the Al_2O_3 ALD film thickness. Power spectral density (PSD) analysis revealed that the ALD smoothing was most effective for surface topographical features with lateral spacings in the range of 10s to 100s of nanometers. The PSD analysis showed that most of the smoothing occurred during the first 1000 Al_2O_3 ALD cycles. Reflectivity studies of silver films deposited on the silicon wafers also demonstrated that Al_2O_3 ALD smoothing increases reflectivity by lowering reflectivity losses attributed to scattering and plasmon absorption.

TF-Contributed On Demand-148 Sliding Properties of a-C:H Coated CFRP on a Metallic Surface*, Akira Chikamoto,* Meijo University Graduate School, Japan*; P. Abraha,* Meijo University, Japan

Carbon Fiber Reinforced Plastics (CFRP) consists of carbon fibers that provide strength and stiffness and a polymer matrix to protect and hold the fibers together. The surface hardness of the polymer and the wear resistance in sliding with other surfaces is significantly low due to the thermal softening of the polymer. A solution to the dual problem of controlling frictional heat and wear resistance of CFRP surface with other materials can increase the application area of CFRP in sliding parts. In this study, we investigated the sliding distance and specific wear of CFRP surface coated with hydrogenated DLC to clarify the effect of hydrogenated DLC on the sliding properties through evaluation of the PV values corresponding to friction heat and wear resistance.

Surface modification of hydrogenated DLC coating is applied by radio frequency plasma enhanced chemical vapor deposition (RF-PECVD) at low temperature processing to generate flexible DLC that can follow the expansion and contraction of polymer surfaces. Among the DLCs that can be coated by the plasma process, soft hydrogenated amorphous carbon (a-C:H) is a good candidate that can follow the elongation of the substrate. Polymer-like hydrogenated amorphous carbon with high hydrogen content (40-60at.%) and significant sp^3 bonds can follow the deformation of the substrate and improve the mechanical properties. However, the sliding properties of polymer-based DLC coatings vary greatly depending on the plasma conditions such as the negative bias voltage to control the temperature rise under the glass transition temperature and maximize the PV values.

In this experiment, hydrogenated DLC coating was applied in varying the negative bias voltage and measured the sliding distance to the glass transition temperature. On the other hand, the specific wear was measured by varying the PV values. The hydrogenated DLC film coated with a negative bias voltage of 500 V showed excellent sliding characteristics. The friction heat due to the sliding distance to the glass transition temperature was longer upon increasing velocity while the specific wear rate showed better wear resistance for increasing pressure. In this presentation, we will explain the effect of hydrogenated DLC coating on sliding properties with metallic surfaces using the obtained experimental PV curves.

TF-Contributed On Demand-151 Tungsten Infiltration of CNT Forests by ALD for Micro-Scale X-Ray Collimators*, **Chase Vanfleet**, R. Cass, R. Vanfleet, R. Davis, R. Vanfleet,* Brigham Young University

Micro-scale collimators were fabricated using carbon nanotube templated microfabrication (CNT-M) and atomic layer deposition (ALD) of tungsten. These collimators were parallel hole arrays 400-1000 microns tall, with square channels 25-200 microns wide and walls 4 microns thick. The micro-scale patterned CNT forest growth provides a 3-dimensional template that is infiltrated with tungsten, a high-density material for X-ray absorption and attenuation. The uninfiltrated CNT forest is pretreated with ozone to increase the nucleation site density. ALD penetration into the CNT forest is limited by diffusion and adsorption, resulting in a penetration depth of approximately 15 microns. Additionally, tungsten concentration decreases from top to bottom of collimator pores, especially those of higher aspect ratios. This gradient can contribute to stresses and distortions in the collimator structure, but these effects can be addressed through template dimensions, forest height, and deposited tungsten thickness. The mechanical properties of the infiltrated forests were measured through resonant frequency and 3-point bending analyses. A Young's modulus of 9±4 GPa was observed. Collimation performance and properties were evaluated on a Bruker Apex 3 X-ray Diffractometer using a Cu k alpha X-ray source. At high tungsten loading (100+ ALD cycles), results fit a simple geometric model for low aspect ratios. However, at high aspect ratios distortions in the collimator structure led to reduced peak X-ray throughput. At low tungsten loads (75 ALD cycles), penetration of X-rays through the collimator walls was observed.

TF-Contributed On Demand-154 Using *In Situ* Electrical Conductance Measurements to Study Mechanisms and Wall Effects During Vapor Phase Infiltration (VPI) Doping of Semiconducting Polymers*, **Kristina Malinowski**, S. Gregory, J. Wooding, Y. Li, O. Hvidsten, A. Jungreis, M. Losego,* Georgia Institute of Technology

This talk will discuss our use of *in situ* electrical conductance measurements to study vapor phase infiltration (VPI) doping of polyaniline (PAni) thin films with $TiCl_4$ + H_2O. Using *in situ* electrical conductance measurements we can readily observe real time changes in film doping during $TiCl_4$ infiltration, water infiltration, and purging steps. We use *ex situ* characterization (UV-Vis-NIR and X-ray photoelectron spectroscopies) to provide support for postulated doping processes observed with *in situ* electrical conductance measurements. Together these measurements allow us to propose more consistent doping mechanisms for various VPI processing conditions. We find that dosing and holding $TiCl_4$ in a chamber where hydroxyl groups are present leads to higher-than-expected acid doping of PAni. Doping with $TiCl_4$ alone should only lead to oxidative doping; thus, the observed acid doping must be the result of reacted byproducts from side reactions with the walls. Interestingly, electrical conductance is also observed to decrease upon the subsequent H_2O dose and hold step. This result is surprising because HCl should be generated in the polymer, leading to an increase in acid doping. This opposite behavior suggest that the polymer is already fully acid doped. In an attempt to remove uncontrolled wall effects, we studied a VPI doping process in which the walls were exposed to trimethylaluminum (TMA) prior to $TiCl_4$ dosing in an effort to passivate the hydroxyl reactive sites. Consequently, when $TiCl_4$ is dosed, the passivated walls do not react with $TiCl_4$ nor form HCl, so only oxidative doping occurs. The *in situ* electrical measurements reveal a 4 times slower increase in conductance for this passivated scheme *vs* the former scheme, suggesting that the uncontrolled acid doping from the wall reactions was mitigated. This reduction in acid doping was further confirmed by *ex situ* spectroscopic characterizations.Ultimately, we demonstrate that *in situ* electrical measurements can assist in the design of multi-step processes for VPI doping of semiconducting polymers.

TF-Contributed On Demand-157 Combinatorial Cu_xNi_{1-x} Thin Film Catalysts for Layer Number Control in CVD Grown Graphene*, **Sumeer Khanna**,* University of Tennessee Knoxville*; M. Stanford , I. Vlassiouk ,* General Graphene Corporation*; P. Rack,* University of Tennessee, Oak Ridge National Laboratory

In this work, we have synthesized a combinatorial library of Cu_xNi_{1-x} alloy thin films via co-sputtering from Cu and Ni targets for catalysts for chemical vapor deposited graphene.The alloy morphology, composition and microstructure were characterized via scanning electron microscopy (SEM), energy dispersive x-ray spectroscopy (EDS), and x-ray diffraction (XRD), respectively. Subsequently, the Cu_xNi_{1-x} alloy thin films were used to grow graphene in a CH_4-Ar-H_2 ambient. The underlying rationale is to adjust the Cu_xNi_{1-x} alloy carbon solubility at a fixed temperature (~ 1000 ^{o}C) to control the graphene layer number as the solubility limit of carbon in Cu is approximately 75 +/- 0.5 ppm and C in Ni is 1.3 at.%.

The energy dispersive x-ray spectroscopy (EDS) analysis revealed that a continuous gradient of Cu_xNi_{1-x} (25.29%<x<82.57%) was achieved across the 100 mm diameter substrate (~0.86%/mm composition gradient) for a film thickness of ~2 µm. High-resolution SEM imaging revealed the as-deposited grain size increased with increasing x and the grain shapes changed from disordered nodular structures to uniform spheres. The XRD spectra confirmed a solid solution was realized and the face centered cubic lattice varied from ~3.52 to 3.58 Å, consistent with the measured composition gradient, assuming a Vegard's relationship. Optical microscopy and Raman analysis of the graphene layers suggest single layer growth occurs with x>68.95%, bilayer growth dominates from 47.56%<x<68.95%, and multilayer (>=3) growth occurs for x<47.56%.

In this presentation, we will overview the combinatorial thin film synthesis and Cu_xNi_{1-x} as-deposited and heat-treated alloy catalyst characterization. We will overview the Raman analysis of the CVD grown graphene layers and review transmission electron microscopy (TEM) data for selected areas. Finally, we will show large area bi-layer graphene can be grown via the thin film catalyst with optimized catalyst composition.

TF-Contributed On Demand-160 Molecular Layer Deposition on Nanofiltration Supports for High Performance Desalination Membranes with Tunable Performance*, **Brian Welch**, O. McIntee, T. Myers, A. Greenberg, V. Bright, S. George,* University of Colorado at Boulder

Molecular layer deposition (MLD) can produce all-organic polymer films in a step-wise fashion with conformality and nanometer-scale thickness control. The MLD process has control over chemical composition and crosslinking and produces films with very few defects. In this work, we demonstrate that MLD is an effective method to fabricate reverse osmosis (RO) desalination membranes. The current methods of fabricating RO membranes are limited in the uniformity and thickness of the active membrane film. Desalination using RO membranes offers one of the most cost effective methods of producing fresh water. RO membranes may be produced by depositing all-organic MLD films on nanofiltration (NF) supports.

Polyamide MLD films were grown on NF270 nanofiltration supports (DuPont) using m-phenylenediamine and trimesoyl chloride as the reactants. The polyamide MLD was performed in a rotating cylinder spatial MLD reactor [1]. The polyamide MLD growth rate was 4 Å/cycle at 115�C at a rotation rate of 20 RPM. This rotation rate corresponds to a reactant residence time of 0.3 s. The growth rate was measured using titanium-sputtered polymer substrates and silicon coupons on the rotating cylinder. The composite polyamide MLD films on the NF supports were then tested for their desalination performance.

Dead-end desalination measurements showed that salt rejection was improved at the cost of lower water flux with increasing MLD cycles. By selecting the number of MLD cycles, salt rejection and flux values could be adjusted to span the performance range between NF membranes and RO membranes (Supplemental Figure 1). Furthermore, composite polyamide MLD films on the NF supports fabricated with 30 or more MLD cycles out-performed commercial membranes in terms of salt rejection. Increased precursor residence times during MLD led to a densification of the polyamide layer. This densification resulted in even higher salt rejection and lower flux (Supplemental Figure 2). Performance was further evaluated by studying the effects of MLD processing temperature, terminal surface groups and desalination pressure.

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TF-Contributed On Demand-163 Insight into Film Growth Mechanisms in Polyurea Molecular Layer Deposition Using New and Combined Precursors*, **Rachel Nye**, S. Wang, G. Parsons,* North Carolina State University

Molecular layer deposition (MLD) has gained momentum recently for use in photolithography, memory devices, and energy storage. This organic film synthesis technique, similar to atomic layer deposition (ALD), relies on sequential, vapor-phase self-limiting reactions to deposit a thin layer of material with thickness and conformality control on the molecular scale. The broad access of MLD to organic precursors enables a wide range of film properties and structures, although the exact relationship between constituent precursors and overall film properties is not well understood. We utilize in situ analysis to explore the impact of precursor structure and growth surface on film growth behavior to improve control over film properties for increasingly demanding microelectronic device applications.

We evaluate four structural polyurea variations consisting of ethylenediamine (ED), 1,6-hexanediamine (HD), p-phenylene diisocyanate (PDIC), and 1,6-hexamethylenediisocyanate (HDIC), the latter of which is novel to the field of MLD. These films are deposited on hydroxylated SiO_2 substrates between 25 and 100C. Growth rate decreases with increasing backbone flexibility, attributed to frequent site-terminating reactions from the flexible monomers. Moreover, the growth rate for these organic films is not linear, but rather decreases according to a decrease in active site density from SiO_2 to the bulk deposited polymer. It is desirable to understand and predict the change in growth rate on different substrates, thus we next consider polymer depositions on various polymer substrates. Here we also observe a thickness-dependent growth regime transitioning from initial to steady growth. The more rigid aromatic films have a higher active site density than the aliphatic films, determined by the decreasing growth rate of aliphatic film deposited on an aromatic substrate as the active site density decreases from initial aromatic surface to bulk aliphatic surface (similar to on SiO_2). On the other hand, aromatic films deposited on aliphatic films exhibit an initially increasing growth rate, where the active site density is increasing during the transition from aliphatic to aromatic surface. These opposing trends in active site density are attributed to differences in relative rates of site generation and site termination, which are determined by growth surface, precursors, and deposition temperature.

Furthermore, we show that this nonlinear growth can be described accurately with a simple kinetic model. This model is also applied to describe growth as a function of deposition temperature. These results are expected to facilitate deposition of new materials with increased accuracy in lithography and area selective deposition applications.

TF-Contributed On Demand-166 2020 AVS Dorothy M. and Earl S. Hoffman Award Talk: Sorption and Desorption of TMA During Vapor Phase Infiltration Into Polystyrene and Poly(Methyl Methacrylate) Thin Films*, **Emily McGuinness**[1], C. Leng, M. Losego,* Georgia Institute of Technology, USA

Vapor phase infiltration (VPI) has emerged as a technique for creating hybrid organic-inorganic materials with unique properties. In VPI, vapor phase metalorganic precursors are sorbed and entrapped within the bulk of a polymeric substrate which is then co-reacted with an oxidant generating a metal oxide. To date, VPI has been used to modify industrially relevant properties including the mechanical properties of polymers, stability of polymers in organic solvents, creation of nanoscale features through copolymer patterning, and more. While the utility of VPI has been clearly demonstrated, the fundamental mechanisms of this process remain ill defined. To expedite experimental discovery and industrial application of this process, an improved understanding of the kinetics and thermodynamics of VPI is necessary. In this presentation, we will establish a new theory of metalorganic precursor sorption during VPI. Specifically, we extract fundamental kinetic and thermodynamic values from sorption-desorption curves generated with quartz crystal microgravimetry (QCM) by monitoring metalorganic precursor mass uptake as a function of time and VPI processing step. By exploring the infiltration of polystyrene with trimethylaluminum (TMA) and water, fundamental models for gas sorption in polymers can be applied to a system where no chemical reactions occur with the polymer. By applying models such as the Berens and Hopfenberg model for gas sorption into glassy polymers and Fick's second law, diffusion and relaxation constants and behaviors of polystyrene when exposed to TMA has been quantified. Establishing these behaviors and fundamental values is key to optimizing VPI processes for specific infiltration depths while minimizing reaction times. To further investigate a system where reactions between TMA and the polymer exist, studies of poly(methyl methacrylate) [PMMA] infiltrated with TMA and water, were performed and fundamental models are applied to the system. The TMA/PMMA system exhibits a temperature dependent shift in reaction mechanism which adds complexity to the sorption-desorption process. For this method, a facilitated transport model probes how the strength of the interaction between TMA and the polymer backbone alters the diffusion of TMA throughout the polymer bulk. Overall, by experimentally validating how fundamental polymer theories can be applied to the VPI process, we establish a new framework for interrogating precursor-polymer systems in VPI that results in key thermodynamic and kinetic parameters integral to experimental design and industrial application.

TF-Contributed On Demand-169 Experimental Study of Plasma-Enhanced Atomic Layer Deposition of SiN on GeSbTe*, **Hamid Razavi**,* University of California at Los Angeles*; M. Shen, J. Hoang, T. Lill,* Lam Research Corporation*; J. Chang,* University of California at Los Angeles

Using $Ge_xSb_yTe_z$ (GST) in phase-change memory (PCM) has been widely investigated as the next generation of non-volatile data storage applications due to its outstanding properties including fast programming capability, good cyclability, and power efficiency. This ternary compound can switch between its amorphous (high electrical resistivity) and crystalline (low electrical resistivity) phases in response to a temperature alteration at high speed.

One of the challenges of GST material integration is to maintain its stoichiometry throughout various processes including deposition, cleaning, and patterning. This problem originates from the intrinsic higher volatility of Ge-containing products compared to those containing Sb and Te.

In this work, Ge is selected as a model substrate for GST to assess the nucleation and growth of SiN by plasma-enhanced atomic layer deposition (PE-ALD) using Bis(t-butylamino)silane (BTBAS; $[NH(C_4H_9)]_2SiH_2$) as the Si precursor and atomic nitrogen generated by a 2.45 GHz coaxial waveguide microwave plasma source nitrogen as a nitridizing reactant. The relative concentration of nitrogen in the N_2 plasma was measured at different plasma operating conditions using optical emission spectroscopy (OES). High-resolution spectral scanning of 740–750 nm for ^4P-$^4S^0$ emission lines was used to determine relative N concentration. N/Si ratio in SiN thin film can be adjusted by changing the N concentration generated by N_2 plasma. The effects of substrate temperature (25 to 160°C), microwave plasma power (25 to 75 W), and the pre-deposition plasma surface treatment on the deposition of PEALD SiN was evaluated. The nucleation and the growth of deposited SiN on the substrates was studied using an in-situ x-ray photoelectron spectroscopy and ex-situ scanning electron microscopy (SEM). The nucleation of Si_xN_y with the ratio of x:y=1:2 on Ge/GeO_2 was confirmed by XPS analysis. The in-situ N_2 plasma was effective for substrate cleaning by reducing C and O concentration from the native oxide layer of germanium. In addition, an increase in the deposition temperature from 25°C to 160°C resulted in a more effective reduction of C and O contaminations and making a higher quality SiN insulating layer on the GST films.

TF-Contributed On Demand-172 A Machine-Learnt Volatility Model for the Rapid Selection of Precursors for Deposition and Etch*, **Simon Elliott**,* Schrödinger, Ireland*; A. Chandrasinghe, A. Chandrasekaran, Y. An, M. Halls,* Schrödinger

Volatility is a key property for vapor-based deposition or etch processes, but one that is difficult to compute from first principles. Here we utilize a machine learning (ML) approach to train surrogate models for pressure-temperature relationships. The first step involves the curation of volatility data from experimental vapor pressure curves for over 1,000 purely organic molecules. A variety of ML algorithms (Random Forest, Neural

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[1] **AVS 2020 Dorothy M. and Earl S. Hoffman Awardee**

Networks etc) are studied in conjunction with different chemoinformatic descriptors and fingerprints. The trained ML model is capable of predicting the evaporation temperatures for 1 Torr and 10 Torr partial pressure of the organic compounds with a mean error of 25 degrees C. We show how a suitable choice of descriptors enables the model to be extended to metalorganic complexes.

The utility of the ML model is illustrated on the following precursor discovery examples. We first present a screening of the volatility of OH-containing molecules for the molecular layer deposition of hybrid organic-inorganic films, where there is still much scope for introducing new volatile organic precursors. As a second example, when developing etching processes, a key criterion is that the etched product should be volatile, and we show how the ML volatility model can be combined with other chemical criteria such as safety constraints or environmental impact of the exhaust gas. The speed of evaluation of the ML model on the computer means that thousands of candidate compounds can be screened per day.

TF-Contributed On Demand-175 Gas Bubble and Blister Formation in Sputtered Thin Film Cadmium Selenide*, Rachael Greenhalgh*, *P. Hatton, V. Kornienko, A. Abbas, P. Goddard, R. Smith, J. Bowers, M. Walls,* Loughborough University, UK

Cadmium Telluride is the most successful thin film photovoltaic technology with manufacturing capacity steadily increasing and currently >6GW. The technology is predominantly used at utility scale for solar electricity generation.The efficiency of cadmium telluride solar cells has been improved recently by adding selenium as a CdSeTe alloy to the front of the device. Diffusion occurs and a graded band-gap absorber is formed to allow the solar cell to extend its use tohigher wavelengths thereby increasing the short circuit current density (Jsc).One way to introduce the selenium is to first deposit a layer of CdSe on to the buffer layer before depositing a CdTe layer by sublimation at the back of the cell.The two layers are then inter-diffused during the cadmium chloride activation process.Pulsed dc magnetron sputtering is an attractive method to deposit the CdSe because it provides high deposition rates, excellent thickness control and uniformity.It is also industrially scalable.Studies using RF sputtered CdSe have reported the presence of voids in the CdSeTe/CdTe devices but the reasons behind their formation have not been understood.These voids are particularly harmful if they accumulate at the junction with the n-type buffer layer. In this paper, we show that the voids are caused by the accumulation of trapped argon which formsgas bubbles during annealing and/or the cadmium chloride activation process.These bubbles can also develop into large blisters causing exfoliation of the device surface and catastrophic delamination.We have used cross-sectional TEM and EDX to characterize the voids following a sweep of the sputter-process conditions including substrate temperature, working gas pressure, target power etc….We propose a mechanism for the bubble formation based on the microstructure of the sputtered CdSe thin films.

TF-Contributed On Demand-178 Chemical Bath Deposition of Cus_X and Sns_X on Functionalized Self-Assembled Monolayers*, Tania Estrada*, *A. Walker,* University of Texas at Dallas

Transition metal chalcogenides have applications including in photovoltaics, optoelectronics, and biomedical engineering. This is because these materials have a wide range of electrical properties which are dependent on their stoichiometry. In this paper we investigate the use of chemical bath deposition (CBD) to selectively deposit copper and tin sulfides on functionalized self-assembled monolayers (SAMs). CBD is an inexpensive, facile solution-based method for deposition of transition metal chalcogenides. We employ three different SAMs with -CH_3, -OH and -COOH terminal groups, and vary the bath pH from pH 9 to pH 12. Using time-of-flight secondary ion mass spectrometry (TOF SIMS) and x-ray photoelectron spectroscopy (XPS), we demonstrate that the stoichiometry of the transition metal chalcogenide deposit is strongly dependent on the substrate chemistry. On -COOH terminated SAMs, Cu_2S is always deposited while on -CH_3 terminated SAMs CuS deposits. In contrast, on -OH terminated surfaces the Cu_xS deposit changes from Cu_2S at pH 9 to CuS at pH 12. Similarly, our data shows that for SnS_x there are also changes in the film stoichiometry. At pH 9 SnS_2 is deposited on -COOH and -CH_3 terminated SAMs while SnS is deposited on -OH terminated SAMs. At pH 10, the stoichiometry of the film switches; SnS deposits on -COOH and -CH_3 terminated SAMs while SnS_2 deposits on -OH terminated SAMs. We discuss the mechanisms of these stoichiometry changes in terms of the interaction of the chalcogenide ion and metal ion precursors with these functionalized organic substrates, and the implications for area selective deposition of these films.

TF-Contributed On Demand-181 Formation of Conformal $Ge_2Sb_2Te_5$ Film by ALD and Tellurization of Ge-Sb Film for Three-Dimensional Phase-Change Random-Access Memory Applications*, Kwonyoung Kim*, *Y. Kim, O. Kim, W. Lee,* Sejong University, Korea (Republic of)

Phase-change random-access memory (PCRAM) has drawn attention as the storage class memory. $Ge_2Sb_2Te_5$ is the representative chalcogenide material for PCRAM, and many studies have been reported due to its fast switching speed and high data retention. $Ge_2Sb_2Te_5$ thin films deposited by sputtering have been used in commercially available cross-point type memory products. With the recent maturation of three-dimensional (3D) NAND technology, 3D PCRAM architectures have also been proposed. Thus, it is necessary to introduce atomic layer deposition (ALD) techniques to form conformal $Ge_2Sb_2Te_5$ thin films instead of sputtering. Most of the reported ALD technologies use supercycles of GeTe and Sb_2Te_3 to prepare low-density amorphous films, resulting in a significant volume contraction due to crystallization during the subsequent thermal processes. In the previous work, we reported a high-density crystallized GeSbTe thin film prepared by ALD of Ge-Sb at a low temperature and subsequent annealing in a tellurium atmosphere. However, the previous work focused on the gapfilling of confined structures for cross-point type devices, and the composition of the thin film was $Ge_3Sb_2Te_6$. In the present study, a $Ge_2Sb_2Te_5$ thin film was formed by controlling the composition of the Ge-Sb film, and step coverage was improved by optimizing the annealing condition in a high aspect ratio pattern for 3D device applications. The composition of the Ge-Sb film was controllable by changing the ratio of the subcycles of ALD GeSb and ALD Sb. We investigated the composition, phase transition temperature, density, roughness, and step coverage of Ge-Sb films with different compositions before and after the tellurization annealing. The $Ge_2Sb_2Te_5$ thin film with excellent step coverage was prepared.

TF-Contributed On Demand-184 About the Importance of Purge Time in Molecular Layer Deposition of Alucone Films*, Hardik Jain*, *P. Poodt,* Holst Centre / TNO, Netherlands

The deposition rate and properties of MLD films are for a large part determined by what happens during the precursor exposure. 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). These alucone films tend to be porous in nature due to which the reactants during their exposure step not only react at the film surface but also tend to infiltrate into the film. The 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 undesirable CVD component alongside MLD in the overall growth. We have investigated the MLD of alucone focusing on the effect of purge time of TMA on the growth kinetics. To avoid any negative impact of the CVD component on the deposition rate and the film's properties, we have also developed a kinetic model to corelate parameters like exposure times, partial pressures, purge times and deposition temperature to the CVD component in the growth. Finally, we show that using a bulkier precursor like DMAI instead of TMA can overcome the problem of precursor infiltration and increase the deposition rate of alucone processes by at least an order of magnitude

TF-Contributed On Demand-187 Nucleation Behavior in Laminate ALD Film Stacks, *K. Holden, A. Valdivia, J. Conley, Jr.,* ***Shane Witsell,*** Oregon State University

Nucleation in ALD determines how many cycles it takes to initiate growth and form a continuous film, and can impact bulk film and growth properties.[1,2] Nucleation has been exploited for the formation of nanoparticles, catalysts, and more recently for area-selective ALD.[3,4] Although sometimes overlooked or even misrepresented in ALD reports,[5] nucleation is also critical for multicomponent ALD and laminate ALD for ultra-thin metal/insulator/insulator/metal diodes.[6,7] Here we demonstrate two types of nucleation behavior in ALD laminate films of Al_2O_3 on Nb_2O_5 and Nb_2O_5 on ZnO.

ALD was performed at 250 °C in a Picosun SUNALE R-150B using H_2O with TMA, niobium ethoxide, or DEZ for Al_2O_3, Nb_2O_5, or ZnO, respectively. Thickness of Al_2O_3 on Nb_2O_5 and Nb_2O_5 on ZnO was measured using TEM and VASE, respectively.

GPC and nucleation delay of Al_2O_3 on six thicknesses of Nb_2O_5 was determined from plots of thickness vs. cycles. The nucleation delay of Al_2O_3

on bare Si is ~0 cycles due to an abundance of surface hydroxyl groups with which the methyl groups readily undergo exchange reactions.[1] Al_2O_3 nucleation delay is increased to 10 cycles for a single cycle of underlying Nb_2O_5, decreasing to ~2 cycles for 20 or more cycles of Nb_2O_5 (Fig. 1). One possible explanation for greater inhibition of nucleation by thinner Nb_2O_5 films may be a partial removal of surface hydroxyl groups. The 1-cycle Nb_2O_5 film is not continuous (as seen by a faint layer in hi-res TEM) and therefore nucleation is not entirely on a pure Nb_2O_5 surface. Increasing the number of underlying Nb_2O_5 cycles eventually forms a continuous surface and the Al_2O_3 nucleation delay decreases and finally saturates.

Nb_2O_5 growth vs. cycles extrapolates to negative cycles for bare Si, indicating "enhanced" nucleation. On 4 and 25 nm of ZnO, nucleation delays are ~0 and ~80 cycles, respectively (Fig. 2). One likely explanation is the ZnO film morphology. For the 4 nm ZnO (27 cycles), crystal nuclei have not completely coalesced, forming a discontinuous arrangement of ZnO nano-islands, as is well-known for the DEZ/H_2O process.[2] For the 25 nm ZnO film (167 cycles), a more continuous ZnO surface results in increased Nb_2O_5 nucleation delay and reduced GPC.

These examples of inhibited and enhanced nucleation emphasize the importance of understanding the early stages of ALD for laminate and multicomponent films. Additional results on other systems will be presented including impact of temperature.

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TF-Contributed On Demand-190 Flexible Low-K SiCOH Thin Films Deposited by Plasma Enhanced Chemical Vapor Deposition of Tetrakis(Trimethylsilyloxy)Silane Precursor*, **William Wirth**, S. Jang, J. Comeaux,* University of Louisiana at Lafayette

The semiconductor industry has used an inter-metal dielectric (IMD) material as an interconnect in integrated circuit (IC) chips. In advanced interconnects, the resistance-capacitance (RC) delay is becoming the main obstacle for the downscaling in the chips. To reduce this delay, low dielectric (low-k, k<3.5) materials have been used in place of traditional silicon oxide (SiO_2 with k≈4.2) while aluminum (Al) has been replaced by copper (Cu) as the metal lines with lower resistivity. On the other hand, there is an increasing interest in flexible materials, which can be used in flexible electronics including flexible displays and lightweight wearable devices. It is important to study the electrical and mechanical stability of the materials for the integration of flexible electronic devices. This study investigated the effect of repeated bending on structural, electrical, and mechanical properties of low-k SiCOH thin films. The SiCOH films were deposited onto ITO/PEN (indium tin oxide on polyethylene naphthalate) substrates by plasma enhanced chemical vapor deposition of tetrakis(trimethylsilyloxy)silane precursor. Deposition parameters varied the RF plasma power from 20 to 100 W at 13.56 MHz. Ar was used as a carrier gas with a flow rate of 18 sccm. Operating pressure was held at 26.7 Pa for the 20 minute deposition. The films were subjected by bending test with up to 10000 bending cycles. Mechanical characterization was performed by nanoindentation testing for the elastic modulus and hardness. Chemical bonds were characterized by Fourier transform infrared (FTIR) spectroscopy, and the atomic concentration was measured by X-ray photoelectron spectroscopy (XPS). The electrical properties including dielectric constant and leakage current were measured by capacitance-voltage (C-V) and current-voltage (I-V) curves, respectively. The prominent chemical peaks of C-H_x, Si-CH_3, Si-O-Si, and Si-$(CH_3)_x$ were identified for as-deposited films from the analysis of FTIR spectra. The changes in their peak intensities and peak area fractions were observed after bending test and related to the electrical and mechanical performance.

TF-Contributed On Demand-193 Low-Temperature Atomic Layer N-Type Si-Doping of GaN via Plasma-Assisted ALD*, **Deepa Shukla**, N. Biyikli,* University of Connecticut

Semiconductor doping processes play a critical role in electronic and optoelectronic devices. The ability to dope semiconductor films is a crucial requirement particularly for light-emitting devices including LEDs and solar cells. For electronic device layers, parasitic resistance is an unwanted effect that is unavoidably present in all electronic devices which needs to be reduced in high electron mobility transistors.Si is the main n-type dopant element for GaN device layers, where Si behaves as shallow donor leading to near ideal ionization at room temperature.

Our previous work on low-temperature grown GaN layers using hollow-cathode plasma-assisted ALD (HCPA-ALD) yielded crystalline films with relatively low impurity content. However, the resistivity values of these polycrystalline films with preferred (002) orientation exhibit beyond device compatibility large resistivity values. While continuing our effort in improving as-grown GaN layers, we aim to incorporate Si dopant atoms into the HCPA-ALD GaN layers to achieve device-level resistivity values.

In this work, GaN is doped with n-type Si-dopant during HCPA-ALD process. The substrate temperature is kept between 120 and 240 °C. The N_2 carrier gas flow is kept at 10 sccm, and Ar-purging gas flow at 50 sccm. The TEG precursor and various nitrogen plasma chemistries including different compositions of N_2, H_2, and Ar gases are used to grow GaN. Si-dopant precursor utilized is the tris (dimethylamino) silane (TDMAS). The optimized growth condition is determined via in situ monitored saturation studies, where the growth-per-cycle (GPC) parameter is noted for different precursor pulse time, rf-plasma power (50 W to 200 W) and plasma-gas chemistries (N_2-only, N_2/H_2, Ar/N_2, Ar/N_2/H_2 at varying ratios). In addition, different plasma compositions studied are (i) Ar/N_2 at 50/50 sccm; (ii) N_2-only at 50 sccm; and (iii) N_2/H_2 at 50/10 sccm. The Hall-effect measurement will be carried out to determine the carrier concentration, mobility, and resistivity in the n-type doped GaN samples. Optical, structural, and chemical properties of the grown n-type dopded GaN films will be characterized via spectroscopic ellipsometry, x-ray reflectivity (XRR), x-ray diffraction (XRD), x-ray spectroscopy (XPS), and transmission electron microscopy (TEM).

TF-Contributed On Demand-196 Investigating the Phase Separation Dynamics and Magneto-Plasmonic Properties in Au_xCo_{1-x} Films and Nanoparticles for Magnetically Enhanced Photothermal Cancer Therapies*, **Reece Emery**, D. Garfinkel, G. Pakeltis, N. Tang, D. Gilbert ,* University of Tennessee Knoxville*; P. Rack,* University of Tennessee, Oak Ridge National Laboratory

Au_xCo_{1-x} thin films with a composition range from ~ 0.8<x<0.2 were synthesized via a combinatorial co-sputtering process from elemental Au and Co targets. The as-deposited films were nanogranular supersaturated solid solutions and various thermal annealing treatments were used to control the phase separation lengthscale in the films. Additionally, sub-20 nm thin films were exposed to ~ 20 ns KrF laser pulses to realize liquid phase dewetting and thus produced nanoparticle arrays. Ellipsometry, optical transmission, and low-loss electron energy loss spectroscopy were exploited to determine the system’s optical properties, while the magnetic properties were measured using a vibrating-sample magnetometer. Energy dispersive x-ray spectroscopy, along with electron, and X-ray diffraction were utilized to correlate the magneto-plasmonic behavior with composition and crystal structure, respectively. Finally, laser system mounted onto a scanning transmission electron microscope was used to photothermally heat the Au_xCo_{1-x} films and observe the phase separation *in situ*. Photo excited electron energy gain spectroscopy was also used to characterize the surface plasmons of the phase separated materials. The magneto-plasmonic bifunctionality of these materials have applications in ultrasensitive biosensing, and biomedical applications such as magnetically enhanced photothermal cancer therapies.

TF-Contributed On Demand-199 Structural and Magnetic Properties of NCuZn Ferrite Films Prepared by Sputtering*, **Roni Paul**, J. Abu-Qahouq, S. Kotru,* The University of Alabama

Ferrite films are used in high-frequency applications due to their low conductivity and lower eddy current losses as compared to metal alloy films. In this work, thin films of $Ni_{0.35}Cu_{0.2}Zn_{0.45}Fe_2O_4$ (NCZF) were deposited on Si substrate using sputtering method at three different substrate temperatures of 25^{o}C, 150^{o}C, and 300^{o}C. The as grown films were annealed at various temperatures (500-800^{o}C) using rapid thermal annealing (RTA). The structural and magnetic properties were studied as a function of annealing temperature using X-ray diffraction and vibrating scanning magnetometer. A field emission scanning electron microscope was used to obtain the film thickness and morphology. The films deposited at 300^{o}C and annealed at 800^{o}C showed the maximum value of magnetization. The results will be presented.

TF-Contributed On Demand-202 Adaptation of Environmentally-Optimized Structural Factors from White Beetle Scales for Enhancing Light Scattering in Synthetic Fibrous Films*, **Bokyung Park**, S. Han, S. Han,* University of New Mexico*; I. Um,* Kyungpook National University, Korea (Republic of)

Title: Adaptation of Environmentally-Optimized Structural Factors from White Beetle Scales for Enhancing Light Scattering in Synthetic Fibrous Films

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Keywords: Light scattering, White Beetle, Anisotropic Structure, Electrospinning

We demonstrate that environmentally optimized structural factors in *Cyphochilus* white beetle scales can be exploited to enhance light scattering strength in synthetic materials. Living organisms in nature have evolved over millions of years to adapt to the environment. The white beetle scale structure is an example of such evolution to achieve exceptionally strong broadband scattering strength, which is an order of magnitude greater than common white papers. The key to such strong scattering is an anisotropic nanoscale fibrillar network structure. While various studies were conducted to understand the structure-property relationship, a model is yet to be developed to capture the underlying physics of white beetle scale's light scattering and translate the understanding to manufacturable man-made structures such as electrospun fibers. Here, we develop a cylinder model to explain light scattering in the complicated fibrillar structure and to determine how closely electrospun structures can approach the scattering characteristics of beetle scales. The cylinder model is used to find optimal values for light scattering and validated by experimental results. By electrospinning, we create nanofibrous films, in which the fibers are randomly oriented in the lateral plane like the internal structure of white beetle scales. We then manipulate structural factors (e.g., fill fraction and fibril diameter) by adjusting electrospin process parameters. We discover that the cylinder model well represents the white beetle scale structure and that the scattering strength in electrospun structures can be enhanced by almost a factor of four by adjusting their structural factors. These findings point to the important role of the structural factors in light scattering optimization and elucidate the underlying physics of the efficient light scattering in white beetle scales. Our work suggests that artificial polymeric nanofibers can be used to achieve exceptionally strong broadband light scattering instead of inorganic white enhancers, such as photonic glasses, in various areas of optical engineering.

TF-Contributed On Demand-205 Halogenated Polymer Thin Film with Ultra-High Refractive Index*, **Ni Huo**, W. Tenhaeff,* University of Rochester

High refractive index polymers (HRIP) are an incredibly important class of materials given their potential applications in optoelectronic devices, such as anti-reflective components for displays, encapsulants for light-emitting diodes, and optical sensors. Because typical commodity polymers possess refractive indexes (RI) in the range 1.3 – 1.7, obtaining polymers with RI greater than 1.8 while maintaining high optical transparency is an important challenge. Halogen atoms such as chlorine, bromine, and iodine have high atomic refractivity ranging from 5.97 to 13.90, making them useful components in the development of HRIPs.

In this work, a series of halogenated polymer thin films with high refractive indexes (n =1.7 - 2.0) and outstanding optical transparency in the visible range, were prepared via a unique vapor phase process – initiated chemical vapor deposition (iCVD). iCVD is a versatile technique that has been used to fabricate a wide range of polymer coatings for many applications. In this study, poly(4-vinylpyridine) (P4VP) films with thickness ranging from 100nm to 1000nm were prepared using iCVD, then treated by halogen vapor to form halogen-containing polymer thin films with high RI. The charge-transfer complex (CTC) formed between P4VP and halogen compounds, prepared by a simple vapor phase infiltration of halogen compounds, increases the RI of the P4VP thin film from 1.58 to 2.0 or higher, while maintaining the conformal and smooth nature of as-deposited thin films. Specifically, the P4VP-I2 complex is demonstrated to have an RI of 2.0 and is transparent above a wavelength of 600nm. In another formulation, P4VP complexed with ICl achieved an RI up to 1.77, while still retaining the outstanding optical transparency throughout visible range. The RI of the halogenated polymer films can be further fine-tuned by controlling the concentration of CTC in the polymer film via copolymerization with other monomers that are inert to halogen compounds. In this work, a series P4VP thin films copolymerized with ethylene glycol dimethacrylate (EGDMA) with RI ranging from 1.50 to 1.98 were prepared.

The formation of charge-transfer complex (CTC) in halogenated polymer thin film was confirmed via both Fourier-transform infrared and UV-Vis spectroscopies. The optical performance of these coatings was characterized by spectroscopic ellipsometer and specular reflectometry. The thermal resistance and environmental stability of these films were also investigated as a function of temperature. The refractive index (RI) of P4VP-I2 film decreased by 16% after 96 hours at 30°C. In comparison, the RI of P4VP-ICl film decreased by 0.56% over 96 hours at 30°C. These halogenated polymer thin films are expected to have wide applications in sensors and optoelectronic devices.

TF-Contributed On Demand-208 Epitaxial Growth of Chalcogenide Perovskite Thin Films by MBE*, **Ida Sadeghi**, K. Ye, M. Xu, J. LeBeau, R. Jaramillo,* MIT

Chemical intuition, first-principles calculations, and recent experimental results suggest that chalcogenide perovskites are an outstanding class of semiconductors. Chalcogenide perovskites feature the large dielectric response familiar in oxide perovskites, but also have band gap in the VIS-IR and strong light absorption [1]. Preliminary results suggest that chalcogenide perovskites feature excellent excited-state charge transport properties familiar in halide perovskites, while also being thermally-stable and comprised of abundant and non-toxic elements. Nearly all experimental results on chalcogenide perovskites to-date were obtained on powder samples and microscopic single crystals; thin film synthesis is in its infancy. The history of complex oxides teaches that advances in understanding and applications will hinge on the availability of high-quality thin films, and that the best film quality and control is achieved by molecular beam epitaxy (MBE).

Here we report the first epitaxial synthesis of chalcogenide perovskite thin films by MBE: BaZrS$_3$ films on LaAlO$_3$ substrates. The composition is confirmed by scanning transmission electron microscopy (STEM): films are stoichiometric and oxygen-free, with an atomically-abrupt substrate/film (oxide/sulfide) interface. The perovskite phase is confirmed by STEM, X-ray diffraction (XRD), and Raman spectroscopy. The films are atomically-smooth over large areas, as evidenced by reflection high-energy electron diffraction (RHEED) measuredduring growth and by atomic-force microscopy (AFM). XRD and STEM reveal two, competing epitaxial growth mechanisms: rotated-cube-on-cube growth with direct bonding, and strain-relaxed growth with a self-assembled buffer layer. Evidence for direct rotated-cube-on-cube growth disappears upon increasing the hydrogen sulfide (H$_2$S) gas supply during growth. The film color, spectroscopic ellipsometry, and photoluminescence spectroscopy demonstrate that the films have strong light absorption with direct band gap near 1.8 eV.

This work sets the stage for developing chalcogenide perovskites as a family of semiconductor alloys with properties that can be tuned with strain and composition in high-quality epitaxial thin films, as has been long-established for other semiconductor materials, while also displaying rich solid-state chemistry and physics familiar in complex oxides. Our methods also represent a revival of gas-source chalcogenide MBE, with potential for impact on research on chalcogenide perovskites and other sulfur- and selenium-containing compounds.

[1] R. Jaramillo, J. Ravichandran, APL Materials 7(10) (2019) 100902.

TF-Contributed On Demand-211 Study the Structural, Optical, Electro-Thermal Properties of Oxygen Dependent Growth Ga Doped ZnO Thin Films for Transparent Heater Applications*, **Jasmine Beckford**, M. Behera, S. Pradhan, M. Bahoura,* Norfolk State University

Thin film transparent heaters (TFTH) are gaining popularity in optoelectronics and a variety of domestic applications, including smart windows, car defrosters, and other devices. In this work, conformal growth and characterization of smooth and high quality TFTH made of gallium doped zinc oxide (GZO) are presented in this using physical vapor deposition. We employed high vacuum Pulsed laser deposition (PLD) technique was used to deposit GZO thin films on glass substrate at different oxygen partial pressure of the growth chamber ranging from 0-10mTorr.Ga doped ZnO in the composition of Ga0.07Zn0.93O target was prepared in the laboratory using Ga$_2$O$_3$ and ZnO as raw powders through conventional solid solution route. Atomic force microscopy reveals that the films are very good quality with smooth surface roughness *<2nm.*Temperature dependent resistivity measurements were carried out using linear four probes methods, and the sample demonstrated low sheet resistance values of *1.8 x 10^-3* Ω.cm.Uv-Vis spectra proved thatthe films showed high optical transparence value of (>85%). GZO transparency thin film heaters demonstrated a consistent and repeatable Joule heating effect, with temperatures reaching 60°C with a low input voltage of 8V and 130°C at 12 V.This research funding could guide future use of GZO as a transparent conducting oxide material for applications in low-cost optoelectronics, as well as lightweight and wearable electronic applications.

TF-Contributed On Demand-214 Molybdenum Cobalt Sulfide Thin Films for Water Splitting Applications*, **Lee Kendall**, G. Zangari , S. McDonnell,* 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.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 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 these issues, this effort will focus on the electrodeposition of $Mo_{1-x}Co_xS_2$ films. Co has been predicted to increase the catalytic activity of MoS_2 due to Co effectively decreasing the unoccupied d orbitals of Mo, increasing the electron density around Mo, and thereby enhancing the H_2/O_2 generation kinetics.Additionally, the Co stabilizes the film by raising the oxygen dissociation barrier and preventing the formation of insulative MoO_3 clusters. We will report on an investigation in the electrodeposition and characterization of varying transition metal concentrations in $Mo_{1-x}Co_xS_2$ and its effect on the physical, electronic, and catalytic properties towards the hydrogen evolution reaction. Through electrodepositing catalytically active $Mo_{1-x}Co_xS_2$ thin films, this effort demonstrates improved water splitting efficiency over current, low-cost materials.

Thin Films Division
Room On Demand - Session TF-Invited On Demand
Thin Film Invited On Demand Session

TF-Invited On Demand-1 Inherent Selective Atomic Layer Deposition Strategies and its Applications*, **Rong Chen**,* Huazhong University of Science and Technology, China **INVITED**

The chemical principal and mechanisms that enable selective atomic layer depositions are gaining rapid growing interests, which have unlocked attractive avenues for the development of novel nanostructures by depositing atoms at desired surface locations. It has found versatile applications in emerging fields beyond semiconductor industry. Yet with the continuing downscaling, it is important to expand approaches for selective ALD with atomic scale precision on nanoscale features. The self-driven selective growth is needed, modifiying specific surface down to atoms, to enable unprecedented capability of tuning the structure-property relationship for emerging applications. In this talk, the inherent selective atomic layer deposition processes will be discussed, including defects modification, selective growth on desired heterogeneity regions, including terraces, step edges, phases etc. of the same material. By choosing the precursors with proper ligands activity, steric hindrance etc., terraces or step edges selectivity can be achieved. The method could control the decoration sites and growth orientations to obtain preferred exposure properties. The developed facet-selective ALD has been used in oxidation of benzyl alcohol to enhance the selectivity and yield of target benzaldehyde products. The selective deposition on the step edges also enhance the nanoparticles' stability under aging treatment, that prevent the atoms at edges from gasifying. The surface originally has local and subsurface irregularity in the lattice matrix, include vacancies, dangling bonds etc. Relies on precursors' preferential adsorptions on those sites, single atoms fabrication can be achieved for highly active CO oxidation catalysis. The selective deposition also enables the defects passivation for photoluminescence applications. The surface defect sites of CsPbBr3 quamtums dots are selectively passivated that the nonradiative decay is effectively suppressed, and extends the exciton lifetime as well as the fluorescence quantum yield. It is a great expansion of ALD beyond semiconductor industry, and helps bridge high accuracy and robustness of bottom up nanofabrication.

TF-Invited On Demand-7 Free-Standing Nanoengineered Functional Oxides Thin Films*, P. Salles, I. Caño,* ICMAB-CSIC, Spain*; R. Guzman,* School of Physical Sciences and CAS Key Laboratory of Vacuum Physics ; University of Chinese Academy of Sciences, China*; W. Zhou,* School of Physical Sciences and CAS Key Laboratory of Vacuum Physics, University of Chinese Academy of Sciences, China*; **Mariona Coll**,* ICMAB-CSIC, Spain **INVITED**

Complex oxides are of great interest for their rich variety of chemical and physical properties including magnetism, ferroelectricity, multiferroicity, catalytic behavior, and superconductivity. Up to date, the preparation of crystalline complex oxide thin films has been mainly limited on substrates that can stand high temperature thermal treatments and on single crystal substrates when epitaxial growth is pursued. These requirements dramatically limit their applicability excluding the possibility to prepare many artificial multilayered architectures to investigate emergent phenomena that arise in thin films and at their interfaces. To tackle this bottleneck, herein, we will present a facile and sustainable chemical route to prepare water-soluble epitaxial $Sr_3Al_2O_6$ thin films to be used as sacrificial layer for future free-standing epitaxial complex oxide manipulation. Two solution processes are put forward based on metal nitrate and metalorganic precursors to prepare dense, homogeneous and epitaxial $Sr_3Al_2O_6$ thin films that can be easily etched by milli-Q water. [1] Thorough investigation of the precursor-solvent compatibility, thermogravimetric analysis and film crystallization is performed. Additionally, we demonstrate the viability of $Sr_3Al_2O_6$to subsequently prepare and transfer a wide variety of atomic layer deposited functional oxides (Al_2O_3, Co_3O_4, Fe_2O_3, $CoFe_2O_4$, $BiFeO_3$) on arbitrary substrates ranging from flexible polymers to silicon substrate. This robust and low-cost procedure could be adopted to prepare a wider family of thin film compositions to fabricate artificial heterostructures and 2D materials with monolayer by monolayer control to go beyond the traditional electronic, spintronic, and energy storage and conversion devices.

[1] P. Salles, M.Coll et al. Adv. Mater. Interf, (2021), 8, 2001643

TF-Invited On Demand-13 A Comparative Study on the Heteroleptic Ti Precursors for ALD of TiO_2: DFT Calculations and ALD Experiments*, H. Kim, R. Hidayat, S. Kim, J. Kim, Y. Choi, **Won-Jun Lee**,* Sejong University, Korea (Republic of) **INVITED**

Titanium oxide (TiO_2) has been an attractive material with interest for various applications, including photocatalysts, optical coatings, and the high-permittivity dielectrics of DRAM capacitors. The atomic layer deposition (ALD) technique is used to deposit thin films with excellent step coverage, accurate thickness control, and excellent film quality. The most common precursors for the ALD of TiO_2 were tetrakis(dimethylamido)titanium (TDMAT) and titanium tetraisopropoxide (TTIP). However, they showed low ALD temperatures because of their insufficient thermal stability. In general, the higher the deposition temperature, the better the physical and electrical properties of the dielectric film. Therefore, Ti precursors with better thermal stability and reasonable reactivity are requested. The thermal stability of the Group 4 metal (Ti, Zr, Hf) precursors can be improved by introducing a "spectator ligand," cyclopentadienyl (C_5H_5, Cp). Stabilizing ability of the Cp ligand can be further enhanced by Me-substitution [1]. In the present work, we compared the thermal stability and reactivity of heteroleptic Ti precursors by density functional theory (DFT) calculations and the ALD experiments. Thermolysis reactions of precursors were simulated, and the ALD temperature windows and the film densities were investigated. The surface reactions of the precursors were simulated, and the saturation dose and step coverage were investigated. Compounds with a different "spectator ligand," such as Cp, Me_5Cp, or linked amido-Cp, were compared. Compounds with different "actor ligands," dimethylamido or methoxy, were also compared. The introduction of a linked ligand or Me_5Cp enhanced the thermal stability compared to introducing a Cp ligand, and the precursor with methoxy ligands showed better reactivity than the precursor with dimethylamido ligands.The underlying mechanisms for better stability or reactivity were described by DFT simulation.

[1]J.-P. Niemelä et al.,Semicond. Sci. Technol. 32 (2017) 093005.

TF-Invited On Demand-19 Refractive Index Control of Highly Anisotropic 2D Materials*, J. Caldwell, **Mingze He**,* Vanderbilt University **INVITED**

Two-dimensional materials are inherently anisotropic – with strong bonding in-plane and weak bonding out-of-plane. Consequently, their optical properties are birefringent, particularly at frequencies of the optically active infrared phonons. At these frequencies, the strong optical anisotropy results in hyperbolicity, where the permittivity tensor along at least one axis is negative, while at least one is positive. Hexagonal boron nitride (hBN) is an exemplary material in this regard. Materials which exhibit hyperbolicity can support volume-confined polaritonic modes, which have a wavelength much shorter than that of light in free space. Such spatially compressed modes have important implications for IR technologies, as they may be utilized to create planar meta-optics that are much more compact than the current state of the art. In particular, 2D materials can be used to realize metasurfaces, capable of shaping both nearfield- and far field light waves for a broad range of applications.

Conventional metasurface designs use geometrically fixed structures, or materials with excessive propagation losses, thereby limiting their potential applications. Here demonstrate that this can be overcome through the realization of a reconfigurable hyperbolic metasurface comprising a heterostructure of isotopically enriched hexagonal boron nitride (hBN) in direct contact with the phase-change material (PCM), such as single-crystal vanadium dioxide (VO2) or GST. Here, the metallic and dielectric domains in PCM provide spatially localized changes in the local dielectric environment that modify the polariton wavelength supported in hBN by a factor of 1.6. Using this platform, we demonstrate the first reduction to practice of in-plane HPhP refraction, and the means for launching, reflecting and transmitting of HPhPs at the PCM domain boundaries. Ultimately, this phenomenon can be used to create planar refractive optics, such as lenses or waveguides, but on length scales far below the diffraction limit. Further, my employing doped semiconductor materials with controllable plasma frequencies, such direct control of hyperbolic polaritons can also be obtained via modification of the free carrier density of the underlying semiconductor

TF-Invited On Demand-25 Microscopic Mechanisms and Applications for Remote Epitaxy of Iii-vs and Heusler Compounds*, Jason Kawasaki,* University of Wisconsin - Madison **INVITED**

Remote epitaxy, i.e., epitaxial growth through a semi lattice-transparent monolayer material such as graphene, has emerged as a promising alternative that circumvents some of the limitations of conventional epitaxy directly on a crystalline substrate. However, the microscopic mechanisms for remote epitaxy remain unclear, in particular, the role of point and extended defects in graphene. In this talk, I will describe our understanding of the mechanisms based on in-situ electron diffraction, photoemission, atomic force microscopy, and photoemission electron microscopy (PEEM). I will begin with experiments on the model system GaAs on graphene/GaAs (001), grown by molecular beam epitaxy (MBE), and describe recent efforts for the growth of Heusler compounds on graphene-terminated Al2O3 (0001). I will also describe one particularly promising application: our observation of strain-induced magnetism in rippled Heusler membranes that are exfoliated from graphene [1]. This work was supported by the ARO (W911NF-17-1-0254), AFOSR (FA9550-21-1-0127), DARPA (0011940523), and NSF (DMR-1752797).

[1] D. Du, et. al. arXiv:2006.10100 (2020)

Vacuum Technology Division

Room On Demand - Session VT-Contributed On Demand

Vacuum Technology Contributed On Demand Session

VT-Contributed On Demand-1 Study on Copper Thermal Spray Coating to Mitigate Electron Cloud Effect in SuperKEKB*, Mulee Yao,* SOKENDAI, Taiwan*; Y. Suetsugu, K. Shibata, H. Hisamatsu, T. Ishibashi, S. Terui,* KEK, Japan

To investigate the effect of the copper thermal spray coating on reducing the secondary electron yield (SEY) and verify its feasibility for accelerators as a countermeasure against the electron cloud effect (ECE), we coated the aluminum substrates (A6063) with copper powder by thermal spraying and measured their SEY, roughness, surface composition and outgassing rate. To establish the best coating parameters for the beam pipes of the SuperKEKB positron ring, we tested different spray conditions, such as particle size of copper powder, substrate surface treatment, spray angle and temperature, and exposure of the coating to electrons. Now we have produced a straight aluminum beam pipe with copper thermal spray coating that can be installed in the SuperKEKB, in order to observe the effect on reducing the ECE in the near future. In the study of the relationship between SEY and roughness, we found that the SEY was inversely proportional to the Sdr (developed interfacial area ratio) or Sa√Spd in the simulation, where Sa is arithmetical mean height and Spd is density of peaks. But the experimental results from the thermal spray sample were not consistent with it. The most probable reason is the limitation of the roughness measuring instrument on the fine and complex surface like thermal spray coating.

VT-Contributed On Demand-4 NIST on a Chip: Photonic and Quantum-Based Sensors for Metrology and Beyond*, Jay Hendricks,* NIST

This talk will briefly outline the NIST on a Chip (NOAC) Program.The unifying theme of the program is aimed at the development of standards and sensors that are small, deployable, that don't require calibration back at NIST.The core the idea of NOAC is that quantum-based measurements, or measurements based on fundamental physics, when employed in sensors and standards, are invariant.In the NIST on a Chip embodiment, the standards lab, or in this case "NIST", is "on a chip"and is powerful to industry and society as it means that large networks sensors (or sensors "integrated" into a product or device) can be deployed and trusted to provide accurate measurements without costly re-calibration. The overall strategy of the program is to first identify working prototype of laboratory scale devices and standards and then, overtime, build prototypes that can be further miniaturized to the chip scale. The successful program means that measurement technology enables high quality measurements to be done "outside the National Metrology Institute" but owed to base properties of nature and are therefore directly tracible to the international system of units known as the SI. Nested within this idea is the development of quantum-based standards for SI traceability. Given time example of lab scale and early prototypes of miniaturized versions will be presented.

VT-Contributed On Demand-7 Improving Temperature Uniformity of Stainless-Steel Components in Thin Film Processing Equipment*, Sudarshan Natarajan,* *D. Sabens, A. Murugaiah,* Momentive Technologies

This presentation outlines the characteristics, potential applications, and benefits of the Momentive Technologies stainless-steel encapsulated thermal leveler. Target applications include temperature uniformity improvement in wafer carriers or pedestals and other internals in chemical vapor deposition (CVD) or atomic layer deposition (ALD) equipment.

Momentive Technologies offers highly crystalline graphite known as thermal pyrolytic graphite (TPG), which exhibits 4X thermal conductivity than copper. Pedestals or wafer carriers or other internals of high temperature and corrosive thin film processing equipment can be manufactured by stainless steel alloys. But the temperature uniformity of these parts are severely limited by the poor thermal conductivity of the alloys. Momentive technologies recently developed stainless alloy encapsulated TPG leveler addresses this issue of temperature non-uniformity. Results of the temperature uniformity improvement and thermal cycle stability of the newly developed leveler are presented.

VT-Contributed On Demand-10 Particle Tracing the ISO Gauge*, Martin Wüest,* *F. Scuderi,* INFICON Ltd., Liechtenstein*; B. Jenninger, A. Stöltzel, P. Kucharski,* CERN, Switzerland*; O. Teodoro, R. Silva, N. Bundaleski,* Nova School of Sciences and Technology, CEFITEC, Portugal*; C. Illgen,* Physikalisch-Technische Bundesanstalt, Germany*; J. Šetina,* Institute of Metals and Technology, Slovenia*; K. Jousten, M. Bernien,* Physikalisch-Technische Bundesanstalt, Germany*; F. Boineau,* Laboratoire national de métrologie et d'essais, France*; M. Vičar,* Czech Metrology Institute, Czechia

In the framework of the EURAMET project 16NRM05 a novel ionization gauge was developed. The goal was to develop a more stable ionization gauge that could be suitable for standardization. The gauge design was completely developed by computer simulations. To increase the reliability of the simulation results, three different software packages were used in parallel (COMSOL, OPERA, SIMION). With these codes the gauge design was refined and experimental features explained. Despite different treatment and methods used in the ionization module of the simulation codes, the results agree very well with the experimental results.

Acknowledgement:

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VT-Contributed On Demand-13 Three-Dimensional Analysis and Design Assessment of the Mast-U Double Beamline Cryogenic Pumping System*, **Xueli Luo**, S. Hanke,* Karlsruhe Institute of Technology, Institute for Technical Physics, 76021 Karlsruhe, Germany*; A. Shepherd,* Culham Centre for Fusion Energy, Abingdon, Oxfordshire, OX14 3DB, United Kingdom*; C. Day,* Karlsruhe Institute of Technology, Institute for Technical Physics, 76021 Karlsruhe, Germany

The MAST upgrade program (MAST-U) is an ongoing nuclear fusion project in Culham Centre for Fusion Energy (UK), aiming to resolve important plasma physics questions and develop advanced divertor designs. In addition, as part of the MAST-U Enhancements project, MAST-U will be used to test steady state operation with current driven by a novel double beamline neutral beam injection (NBI) system. With one axial beamline and one off-axial beamline at 10.6 degrees, this unique design could have greater possibilities and flexibilities in the plasma heating, control and diagnostics.

Fig. 1. Sketch of the MAST-U double beamline NBI system design.

However, as shown in Figure 1 (Please see the supplemental file Figure_1.pdf), this novel NBI system is very complex with many sub-systems. The focus of this paper is the analysis and design assessment of its cryogenic pumping system. Two aspects were systematically studied by simulations with the test Monte Carlo simulation code ProVac3D developed in KIT. First, the dependency of the density profiles along the double beamlines to the in-vessel cryopump was obtained by changing the capture coefficient of the cryopump as a whole in the simulation. Combined with simulation results using the MCNP code, we can estimate the total pumping speed needed to fulfil the requirement of the density profiles. Secondly, different configurations of the cryopump were simulated and a conceptual design, which could deliver the right total pumping speed, was proposed. In order to simulate such a complex system and have high precision for so many simulations in reasonable computation time, all simulations were carried out in supercomputer Marconi-Fusion by using 2560 cores in parallel to simulate 10^{11} test molecules. Obviously, the simulation results obtained in this study will be extremely useful to the success of the challenging tasks of MAST-U.

ACKNOWLEDGEMENTS

This work has been carried out within the framework of the EUROfusion Consortium and has received funding from the Euratom research and training programme 2014-2018 and 2019-2020 under grant agreement No 633053 and from the RCUK [grant number EP/T012250/1]. This work was partially supported by the EUROfusion project VAC_ND in the supercomputer MARCONI-FUSION at CINECA, Italy. The views and opinions expressed herein do not necessarily reflect those of the European Commission.

VT-Contributed On Demand-16 Cost Description and Characterisation of Gases used in immiscible gas Enhanced Oil Recovery processes (IGEOR)*, **Ofasa Abunumah**, P. Ogunlude, E. Gobina,* The Robert Gordon University, UK

The cost implication of gases used in the oil industry has been characterised through data mining and experimentally. About 70% of oil is trapped in reservoir pores globally due to the limitation of primary oil recovery processes. Consequently, certain gases are injected into reservoir pores to displace the trapped oil in a process calledImmiscible GasEnhanced Oil Recovery (IGEOR). Common gases injected are CH_4, N_2, Air & CO_2. The flow mechanisms, such as surface energy, permeability and momentum have been extensively studied by investigators. However, only a few studies have implicated or coupled injected gas cost. No experimental investigation that simultaneously studies the 4 commonly used gases. Nevertheless, the injectant cost is a major part of the operating expense (OPEX) cost centre.It is expected that the gas cost competitiveness of the gases would aid reservoir screening and gas selection in IGEOR applications. Therefore a study is needed to bridge this knowledge gap. From the literature review, it was indicated that the displaced oil is proportional to injected gas volume. It is therefore expected that competition could be tied to gas dynamics in pore surfaces for the respective gases. e

Methodology and Materials

Materials: 5 analogous reservoir porous core samples with different structural parameters, such as micro and macro surface area. 4 IGEOR gases (CH_4, N_2, Air, CO_2) were selected.

Operating Condition**:** Temperature range 293-673K andPressure range 20-300KPa.

Procedure: Gas was injected into the core samples at a set pressure and temperature. Permeate flow rates, temperature and pressure collected as steady state.

Data ming : 353

Experimental Data: 1,097 runs and 8,777 data.

Gas Cost Types**:** Market, Field and experimental gas cost

Result

Analyses of the field and experimental data show thatIGEOR gases can be characterised. All three cost types were found to be strongly correlated to the 6 gas thermophysical properties (R^2).It was found that **CO_2**is the least expensive gas for all 3 gas cost categories, and thus the most competitive. The **Air** EOR process is the most sensitive to cumulative injectant cost.The slope of the graph between gas cost and properties indicated that 9 of the relationship are inversely correlated with the gas properties, while 8 are positively correlated.

Market cost CO_2 > Air> N_2 > CH_4.

Field project gas cost:CO_2 > Air> N_2 > CH_4.

Experimental project gas cost: CO_2 > N_2 > Air > CH_4..

Contribution to Practice: Engineers can apply this knowledge to select the best IGEOR gas for a given reservoir or porous surface. The discovered competitiveness of CO_2 would further incentivise the Carbon Capture and Sequestration (CCS) programmes to reduce greenhouse gases.

VT-Contributed On Demand-19 Vacuum level Sensing Using Optical Refractive Index*, **Kevin Douglass**, J. Ricker,* NIST

Towards the goal of quantum-based traceability of the Pascal, NIST has developed an optical pressure measurement system where traceability is achieved through accurate quantum mechanical calculations of the refractivity virial coefficients of . To bridge the gap in quantum standards between the NIST Fixed Length Optical Cavity (FLOC) and the Cold Atom Vacuum Standard (CAVS) we are pushing the limits in low pressure sensing. We will discuss recent results and ultimate low-pressure limit.

VT-Contributed On Demand-22 Simulation of the Operation of an Ion Pump*, **Tiziano Isoardi**, P. Manassero, L. Bonmassar,* Agilent Technologies, Italy

An ion pump is a system that is capable to produce the ultra-high vacuum. The basic element of this pump is the Penning trap which confines free charged particles in a cylindrical space. This can be done using a combination of an electrostatic-multipolar and a magnetic-dipolar field which allows to trap electrons and to accelerate ions towards one of the two cathodes. The ultra-high vacuum is reached because the ion-cathode collisions generate sputtering phenomena of chemically active Titanium film on anode to which gas molecules from the trap are attached. The process is fed by electrons generated by secondary emissions due to the ion-cathode collisions. These electrons have an elevated total energy (equal to the potential of the cathode) with respect to the ionization potential that allows them to ionize gas molecules more than once until they lose all their energy forming a non-neutral plasma. This mechanism should lead to an exponential increase of the current until the complete emptying of gas molecules, but actually the current stabilizes almost immediately (tens of milliseconds). This means that there is some phenomena that prevent the current exponential growth.
In order to investigate the current behavior, we studied all phenomena that occur inside the pump through repeated Monte Carlo simulations of single electrons inside the trap, by studying all the single charge interactions. It is known that in a non-neutral plasma there is a maximum charge density that can be achieved which depends on the magnetic field magnitude and on the single charge mass. This is called Brillouin limit and can be easily calculated. So we built simulations at the Brillouin limit approximating the plasma as an electrically charged cylinder (taking into account the influence of plasma on the electric field) considering steady-states at different pressures of a single gas (N2 or H2). After that we built a parameterization to calculate the ionization frequency for a single electron that we used to obtain the current at the cathodes. The current values resulting from simulations closely match the experimental data (see attached Fig.1-3). According to the results of the simulation the plasma absorbs a large fraction of the energy of the free electrons generated at the cathode until they can not ionize the gas molecules. This means that the energy loss in the plasma is responsible for the saturation of the current. When the Brillouin limit is reached the current is stabilized to a value that depends essentially only from the

density of the gas and decreases together with the residual pressure of the gas in the trap.

VT-Contributed On Demand-25 Experimental Characterization of a NEG Pump of Novel Size - A Step to its Application in the DEMO Neutral Beam Injectors*, Stefan Hanke*, *C. Day, T. Giegerich, X. Luo,* Karlsruhe Institute of Technology (KIT), Germany*; F. Siviero, M. Mura, A. Ferrara, E. Maccallini, P. Manini,* SAES Getters, Italy*; E. Sartori, M. Siragusa, P. Sonato,* Consorzio RFX, Italy

A fusion reactor requires powerful heating systems among which the neutral beam injectors (NBI) are the most powerful ones. Operation of NBI systems requires very high pumping speeds in the order of several 1000 m^3/s at relatively moderate pressures of 0.02 Pa to manage the high gas flux in the neutralizer part of the NBI. In the past large customized cryopumps were used. A very promising concept for future NBI applications is based on high capacity getter materials. The material candidate is ZAO® developed by SAES Getters, Italy, providing a performance for the pumping of hydrogen approximately two orders of magnitude higher compared to conventional getter materials.

In a systematic technology development over 6 years, the concept of a NEG pump for NBI was developed within the European Fusion Programme to develop a demonstration fusion power plant (DEMO). It started with the comprehensive characterisation of the material and its properties, in particular at pressures which were significantly higher than in previous UHV applications of getter materials. With the time the knowledge was expanded not only regarding pumping and regeneration characteristics of ZAO® itself but also concerning the heating, thermal management, assembly to larger units for scalability and control of these units during operation. The recent step was the design, manufacturing and operation of a NEG pump which is of relevant size to answer all the DEMO NBI relevant questions, to demonstrate the use of ZAO® in a large pump and to confirm the scalability of the chosen design.

The resulting NEG pump of novel size contains 16 kg of getter material, it was tested in the dedicated test facility TIMO at KIT. The paper describes the design of the pump and presents the experimental results, in particular a systematic investigation of sorption characteristics (depending on pressure, gas flux, getter temperature, loading of the getter with gas) and the regeneration behaviour.

VT-Contributed On Demand-28 Shenzhen Synchrotron Radiation Facility Project*, Dongbai Sun*, *G. Liu, R. Si, Y. Cui, B. Yang, Z. Zhou,* Institute of Advanced Science Facilities, Shenzhen, China

A new synchrotron radiation facility is currently in the planning stage and will be constructed in Shenzhen, China, by the Institute of Advanced Science Facilities, Shenzhen（IASF）. The proposed synchrotron light source consists of a 0.2 GeV linac, a full energy booster ring, and a 3 GeV fourth-generation diffraction-limited storage ring which is based on a seven-bend achromat (7BA) to achieve a low emittance of <100 pm·rad. It delivers X-ray synchrotron radiation with a broad range of energies and a brightness in the order of 10^{21} phs/sec/mm^2/$mrad^2$/0.1BW. Besides, 27 beamlines of various methods covering scattering/diffraction, spectroscopy, and imaging have been proposed for the primary phase. The new synchrotron light source is believed to be one of the most essential large-scale science and research facilities in Shenzhen and provides a fundamental platform to serve researchers around the world, and to contribute to industrial development in China's Greater Bay Area.

VT-Contributed On Demand-34 Progress Towards 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 (NIST)

We present our progress towards a comparison of NIST’s cold atom primary vacuum standard and a dynamic expansion vacuum standard. The cold atom vacuum standard (CAVS) converts the loss rate of atoms from a magnetic trap to a vacuum pressure using *ab initio* calculations of the quantum atom-molecule collision cross-section. To validate the CAVS, we have constructed a new flowmeter and dynamic expansion system that can produce low-uncertainty pressures in the ultra-high-vacuum range that is required for atom trapping. We present initial studies of systematics in both the CAVS and flowmeter. We will also discuss prospects for comparisons of both the CAVS and flowmeter to deployable quantum vacuum sensors.

VT-Contributed On Demand-37 NIST's New Flowmeter for the Extremely-High Vacuum*, Stephen Eckel*, *D. Barker, J. Fedchak, E. Newsome, J. Scherschligt, R. Vest,* NIST

At NIST, we have been developing a new, fully-automated, low-outgassing, constant-pressure flowmeter capable of measuring flows to better than 0.5% over the range from 10^{-13} mol/s to 10^{-9} mol/s. While based on the design of the constant-pressure flowmeter used at NIST to calibrate leaks and high vacuum and ultra-high vacuum pressure gauges, our design incorporates several novel features. To achieve measurement of such low flows, our design uses both small variable volumes (<15 mL each) and ultra-small displacements (0.25 mL max). By constructing our variable volumes from low outgassing materials like titanium and designing the flowmeter to be fully bakeable, we achieve <10^{-15} mol/s outgassing rates. The leak that generates the flow is a stainless steel sintered standard leak element. We measure its stability and its conductance (approximately 26 nL/s for N_2) over 4 decades of pressure. We present comparisons to our current flowmeter over the overlapping operating range of about 10^{-11} to 10^{-9} mol/s. When coupled to an orifice flow standard with a 40 L/s conductance for N2 and a 99/1 flow splitter, the combined system can generate partial pressures as low as 10^{-11} Pa, extending NIST’s measurement capability into the extremely-high vacuum (XHV) regime. The first application of the flowmeter will be to measure loss rate coefficients of the newly developed cold-atom vacuum standard (CAVS).

VT-Contributed On Demand-40 Jefferson Lab Injector Beamline Upgrade*, Marcy Stutzman*, Thomas Jefferson National Accelerator Facility

Jefferson Lab is in the midst of an upgrade of the injector beamline. The upgrade has several goals, all of which support upcoming high profile parity violation experiments such as SOLID and Moeller. First, we are developing several paths toward a higher voltage electron source. With highly polarized beam at 200 keV out of the electron gun rather than the current 130 keV operational voltage, the Coulomb repulsion effects in the beam will be minimized, and photocathode damage due to ionization within the cathode/anode gap can be mitigated. Secondly, the only warm RF accelerator cavity at CEBAF, the Capture, and the first SRF accelerator cavity, called the quarter cryo module, will both be replaced by a graded SRF booster module. The booster has two graded cavities to accelerate non-relativistic electrons from the polarized source to energies up to 10 MeV. However, the higher gun voltage of 200 keV is required for this booster to work well. Finally, in support of these upgrades, the entire injector beamline has been redesigned, and the vacuum upgrades for this system and their impact on the performance of the electron source will be discussed.

VT-Contributed On Demand-43 Gas Transmission Rate of Elastomer Seal With a Divided Back-Up Ring Seal*, Masaharu Miki*, *Y. Miki,* EM Technical Lab Inc., Japan

It was presented in the last AVS (VT-TuP4) that the elastomer seal with the back-up ring seal has very low Helium gas transmission rate, which is about less than 10% of the case without the back-up ring seal. Then divided back-up ring seal which is made of some parts was studied. That is because it is less manufacturing cost than non-divided back-up ring seal, especially, in case that the shape of elastomer seal is not a circle but a complicated shape like a horseshoe.

Air gas transmission rate of an elastomer seal with a divided back-up ring seal was evaluated from the ultimate pressure measured. It was found that the divided back-up ring seal has the same performance as a non-divided back-up ring seal. And when a divided back-up ring seal has some space between the parts, it gets worse performance according to the amount of the space. It means that when it has little space between the parts, it gets about 100% performance of a non-divided back-up ring seal, and when it has 10% space of all, it gets about 90% performance of a non-divided one.

Performance of divided back-up ring seals which have some space between the parts were measured and a model to explain the performance of the back-up ring seals has been constructed.

Furthermore, performance of some divided back-up ring seals which are made of some different materials are evaluated.

VT-Contributed On Demand-46 Thermal Evaluation of a Fixed Length Optical Cavity Pressure Standard*, Jacob Ricker*, *J. Hendricks, K. Douglass,* NIST

Over the past few years, NIST has constructed and tested several Fixed Length Optical Cavity (FLOC) Pressure Standards for measuring gas pressure using refractometry. This refractometry technique has been shown to have similar uncertainty to the current NIST primary standards.

However, to achieve this performance they must have uncertainties of temperature measurements on the order of 1 mK. This is easy in a static environment; however, pressure standards need to be able to measure more than one pressure, so pressurization/compression/flow of gas molecules is required. The NIST Fixed Length Optical Cavity (FLOC) pressure standard was designed to accommodate pressure changes while being able to accurately determine the temperature of the gas molecules and glass cavity by using a Platinum Resistance Thermometer (PRT).

From the ideal gas law and thermodynamics, we can estimate the temperature rise due to pressurization of the gas molecules to increase the temperature by 120 K when going from vacuum to atmospheric pressure. However, due to the small heat capacity of gas this quickly dissipates into the surrounding environment.This results in a small, but measurable temperature rise that is significantly larger than our uncertainty.Physical measurements and computer modelling were used to predict the temperature of the FLOC and allow placement of a PRT to provide accurate measurements of the gas temperature to within an uncertainty of 0.5 mK.

VT-Contributed On Demand-49 Stability of Bakeable Capacitance Diaphragm Gauges*, Julia Scherschligt*, *D. Barker, S. Eckel, J. Fedchak, E. Newsome,* NIST

Capacitance diaphragm gauges (CDGs) are workhorse transfer standards for NIST and other metrology labs around the world. Here, we present a stability study of bakeable CDGs, which are useful in vacuum systems with low outgassing or base pressure requirements. In our studies, a set of three bakeable CDGs was baked in a vacuum furnace at 450 C for about 20 days to reduce hydrogen outgassing. After assembly into a NIST transfer standard, the CDGs were baked again at 110 C to reduce water outgassing. After the initial 450 C bakeout, we found that the calibrations of the CDGs shifted by about 15%. However, after the first 110 C bakeout, the CDGs calibrations remained extremely stable, with <0.2% (k=2) change after each subsequent bake. We performed additional tests, which included dropping a 10 kg weight from a height of 30 cm nearby the gauges, venting the system, completely disassembling, sonicating with acetone and ethanol, and reassembling the system. With this expanded regimen, the gauges drifted further, but no more than 0.6% (k=2). These bakeable CDGs are thus remarkably stable, provided they are temperature stabilized when being used. They now form the transfer pressure standard for our new extremely-high vacuum (XHV) flowmeter, being developed as part of our new cold atom vacuum standard (CAVS) program.

VT-Contributed On Demand-52 Outgassing of A36 Carbon Steel Vacuum Chambers*, James Fedchak*, *J. Scherschligt,* NIST-Gaithersburg

A36 steel is a low-carbon (mild) steel commonly used as a structural steel in the US. Secondary refining processes reduce the hydrogen content in mild steel, making these steels excellent candidates as materials for ultra-high vacuum chambers because of their potential to be low-outgassing.Previously we measured and compared the H_2 and water outgassing rates for 7 identical vacuum chambers constructed of common vacuum materials and heat treatments: 304L, 316L, 316LN-ESR (electro-slag re-melt), titanium, aluminum vacuum-fired 316L, and vacuum-fired 316LN-ESR. These chambers are of identical geometry and are from the same manufacturer. In the present study, we measure the hydrogen and water outgassing rate of an A36 chamber with similar geometry to these 7 chambers.We show that the A36 chamber produces one of the lowest outgassing rates compared to any of these vacuum materials.Thus, A36 may be an excellent choice for ultra-high or extreme-high vacuum applications.Compared to stainless-steel such as 304L or 316L, mild steels are more corrosive and magnetic, but the are inexpensive, have excellent properties for welding and machining, and, as we will show, have excellent outgassing properties.This makes them a good candidate for large vacuum systems such as future gravity wave detectors. In this presentation, we will present outgassing results for the A36 chamber and compare these results to the seven other chambers mentioned above.

VT-Contributed On Demand-55 An in-Situ and in-Vivo Characterization Facility for Ion-Gas-Neutral Interactions With Surfaces (IGNIS-2) Under Fusion-Relevant Vacuum Conditions*, Ethan Kunz*, *C. Jaramillo, H. Schamis, M. Parsons, S. Kolecki, M. Fredd, C. Smith, M. Nieto, J. Allain,* Pennsylvania State University

The study of plasma-facing materials (PFMs) in the field of fusion plasma material interaction research involves testing new materials hypothesized to sustain the intense neutron radiation, particle flux, and heat flux of future plasma-burning thermonuclear fusion reactors. Studies involving long-term evaluation of tokamak first wall materials encounter issues with contamination when vacuum is broken on the system and the samples are transported for ex-situ analysis. Therefore, there is a need for facilities capable of simulating key aspects of the fusion environment and analyzing the surface morphology and chemistry of the sample without the necessity of exposure to the ambient environment. However, relevant vacuum conditions that mimic fusion devices are critical to enable interpretation in ex-vessel facilities designed to test and qualify candidate PFMs including background ambient pressure (partial H2O), working gas pressure (D2 at mTorr ranges), wall conditioning (e.g. B, Li) and radiative gas shielding (e.g. N, Ne).

In this work, we present the design of the Ion-Gas-Neutral Interactions with Surfaces (IGNIS-2) facility, currently being built at the Pennsylvania State University. IGNIS-2 is the fourth generation of a series of advanced experimental surface science facilities developed by Allain et al. [1]. Surface modification and ion beam irradiation with ion energies ranging from 50 to 5000 eV and current densities up to 7 mA cm-2 will be performed in this facility. IGNIS-2 will use in-situ characterization to accurately study the surface evolution under exposure to simulated fusion conditions. Characterization techniques include high-pressure X-Ray Photoelectron Spectroscopy (XPS) using a monochromated X-Ray Source, Ion Scattering Spectroscopy (under forward and backward scattering configurations), UV-Vis-NIR reflectance spectroscopy, Multi-Beam Optical Stress Sensor (MOSS), mass spectrometry, and in-situ erosion measurements.

IGNIS-2 will be composed of multiple vacuum stages which will be interconnected via a subway system that will allow sample transfer within stations in-vacuo, retaining the characteristics of the modified surfaces without exposure to air and contamination. The system will also be integrated with a glovebox with in-vacuo capabilities for the preparation of samples for air sensitive processes. Additional stations in the system will host capabilities for thin film deposition and liquid metal application, including a lithium dropper and contact angle measuring station designed in conjunction with the NSTX-U Liquid Metal research being conducted at Penn State.

[1]Allain, J.P., Nieto, M., Hendricks, M.R., Plotkin, P., Harilal, S.S., Hassanein, A. (2007): Review of Scientific Instruments, 78, 11, 113105.

Vacuum Technology Division
Room On Demand - Session VT-Invited On Demand
Vacuum Technology Invited On Demand Session

VT-Invited On Demand-1 Small Diameter NEG Coated Vacuum Chambers by Copper Electroforming*, Lucia Lain Amador*, CERN, Switzerland **INVITED**

Non-evaporable getter (TiZrV) thin film coatings provide ultra-high vacuum conditions in particle accelerators. They are deposited on the internal walls of the vacuum chambers, transforming them from a gas source into a chemical pump. The trend in electron accelerators design consists in approaching the poles of the steering magnets close to the electron beam. This implies reducing the magnet aperture and using very small diameter vacuum pipes [1]. The application of physical vapor deposition (PVD) in such small diameter chambers becomes then very difficult. The aim of this work is to develop a novel procedure of coating/assembly, using a sacrificial aluminium mandrel as substrate of the thin film together with the creation of a surrounding copper chamber by electroforming [2]. As low as 3 mm diameter coated vacuum chambers were successfully produced using this method. After process optimization, TiZrV getter coating showed a good H_2 pumping performance with slightly delayed activation temperature compared to reference NEG coating values.

[1] C. Steier et al., Proceedings of IPAC, Richmond, USA p. 1840 (2015)

[2] L. Lain Amador, P. Chiggiato, L. M.A Ferreira, V. Nistor, A. T. Perez Fontenla, M. Taborelli, W. Vollenberg, M-L Doche, J-Y Hihn, J. Vac. Sci. Technol. A, 36, 021601 (2018)

VT-Invited On Demand-7 Vacuum Technology for Fusion Research*, Christian Day*, Karlsruhe Institute of Technology (KIT), Germany **INVITED**

Vacuum technology is of paramount importance for the design and operation of nuclear fusion devices. Since the start of the first tokamak and stellarator machines in the 60s, vacuum requirements in the harsh fusion environment turned out be design driving. One has to know that, contrary to the accelerator community, where there is a quest for lowest pressures, the pressure requirements in fusion (during the plasma pulse) are relatively moderate (1 Pa range). The pumping speed challenge in fusion, in particular for the larger devices, is not driven by low pressures but comes from the high throughput needed to compensate for the low burn-up of the injected deuterium-tritium fuel.

The first lab-scale machines triggered the development of high throughput turbomolecular pumps. With increasing size, pumping speed requirements became larger and larger. Nowadays, most medium-size fusion devices are equipped with cryogenic pumps. A highlight of this technology is ITER, where the use of tritium poses additional requirements on the vacuum system design.

The next step after ITER, then producing its own tritium and providing electricity to the grid, will be a demonstration fusion power plant (DEMO), the pre-conceptual design of which is under elaboration in different places on the world. On DEMO scale, accumulation pumps would build up excessive tritium inventories which imply regulatory issues. This is why a R&D programme has been launched in Europe to develop alternative pump technology.

The paper will introduce in how the requirements and challenges have evolved over the last five decades of nuclear fusion vacuum technology. Examples will be given for turbomolecular and cryogenic pumps. The DEMO development programme which looks into tritium-compatible mercury driven diffusion and liquid ring pumps as well as high capacity getter pumps will be reviewed and recent highlights be presented.

VT-Invited On Demand-13 Innovations in Gauges and Gas Analysis*, U. Bergner,* VACOM, Vakuum Komponenten & Messtechnik GmbH, Germany*;* ***Klaus Bergner,*** VACOM Vakuum Komponenten & Messtechnik GmbH, Germany **INVITED**

Due to the rapidly advancing digitalization, many B2B and B2C products are experiencing increasing miniaturization to make them more robust, more powerful and require less energy. At the same time, these products are expected to have increased functionality and flexibility. Typical examples are computer chips, OLEDs or smartphones. These products are manufactured by complex equipment. Key function is in first step to make grown complexity visible and in second step to become proficient with it. This is the only way to reach high yield and first time right rates as well as high reproducibility. Hereby many components, which are usually out of focus, are very important; vacuum measurement sensors. In our contribution we describe the current development of partial- and total pressure measurement technology including innovative solutions.

VT-Invited On Demand-19 Quality and Regulatory Issues for Vacuum Technology in Nuclear Power Plants*,* ***Charles Smith,*** US ITER / ORNL*; A. Buckley,* US ITER **INVITED**

The ITER Project is a collaboration between China, the European Union, India, Japan, Korea, Russia, and the United States to build the world's largest tokamak, a magnetic fusion device that will prove the feasibility of fusion energy on a large scale. The device incorporates a large, multi-function vacuum system as part of its primary systems. This will be the first such vacuum system which must be designed to meet the requirements of a nuclear regulatory body. US ITER Project Office (USIPO), which is managed by UT-Battelle on behalf of Oak Ridge National Laboratory for the US Department of Energy, is responsible for the design, fabrication, and delivery of major subsystems, including the Roughing Pump System (RPS) and the Vacuum Auxiliary System (VAS) to the ITER site in Cadarache, France.

Quality and regulatory compliance are of paramount importance to ensure the safe and reliable operation of ITER. As such, the vacuum system is subjected to the requirements of ASME B31.3 and must also undergo review in accordance with the European Pressure Equipment Directive (PED). All fabrication of bespoke components must undergo enhanced surveillance and monitoring to ensure it will perform as required in this challenging regulatory environment. As US ITER supplies equipment to the ITER Project construction site in Cadarache, France for integration, contracts are awarded across the globe. Ensuring compliance is an added challenge when working with a variety of 'equivalent' codes which vary based on the version year cited, differing ways to define qualified personnel, use of different unit systems, and adapting commercially available vacuum technology to meet the rigorous regulatory requirements for an operating nuclear power plant.

This presentation will discuss the quality assurance and regulatory challenges associated with a first of its kind system, the challenge of ensuring the implementation of an ITER approved quality program using a variety of standards and codes, and methods by which the USIPO has adapted its on-site surveillance program to ensure the production of quality hardware during the Covid-19 pandemic.

VT-Invited On Demand-25 Progress in the Construction of the ITER Vacuum System and Advancement in Vacuum Technologies for Fusion*,* ***Robert J.H. Pearce,*** *I. Banerjee,* ITER Organization, France*; J. Benet,* Fusion for Energy, Spain*; B. Boussier, J. Buckerfield,* ITER Organization, France*; F. Canadell,* Fusion for Energy, Spain*; F. Chitu, A. Cobalt, M. Dremel, S. Giors, G. Godia, S. Hughes, E. Quinn,* ITER Organization, France*; C. Smith,* US ITER Project*; A. Teissier,* Fusion for Energy, Spain*; D. Williamson,* US ITER Project*; L. Worth,* ITER Organization, France **INVITED**

ITER is under construction in the south of France in order to demonstrate the feasibility of fusion as a clean power source. It is one of the world's largest scientific and engineering collaborations. The civil structures have progressed, allowing the start of installation of very large vacuum vessels, in-vacuum components and vacuum piping networks.

The ITER vacuum system will consist of a number of large volume vessel systems including: the Cryostat (~ 8500 m3), the Torus (~1330 m3), the Neutral Beam injectors (~180 m3 each) and a large number of lower volume systems. The Vacuum System forms an integral part of the Fusion Fuel Cycle, streaming all gas originating or injected into the tokamak, through the Roughing Pumping System, to the other Tritium Plant processing systems.

The technology of the Vacuum Systems is particularly driven by ITER's fusion power operational phases, where gas streams dominated by hydrogen isotopes will be pumped in a magnetic and ionizing radiation environment. More than 90% of the vacuum system will however be installed and operational for the First Plasma phase.

An overview of the ITER construction is given with details of the challenges and solutions for assembling the UHV systems whilst completing civil works.

New technological developments, to facilitate the demanding vacuum and pumping duties coupled with safe confinement of radioactive/tritium inventories, are highlighted with results from the qualification programs for: in-vacuum nuclear dust filtration, large demountable rectangular UHV metallic sealing, tritium compatible mechanical vacuum pumps, cryogenic pumps, vacuum/cryogenic valves, vacuum instrumentation and vacuum leak localization techniques.

The paper will show spectacular progress in the construction of ITER and in the advancement of vacuum fusion technologies. Confidence in the vacuum system design and operability for both the ITER first plasma and fusion power phases will be demonstrated.

VT-Invited On Demand-31 Overview of the Outgassing Behavior of Metals, Polymers and Ceramics*,* ***Katharina Battes,*** *C. Day, V. Hauer,* Karlsruhe Institute of Technology (KIT), Germany **INVITED**

For every vacuum system the outgassing behavior of the applied materials has an impact on the pump down time and the minimum achievable pressure. Especially, at large systems or if low pressures are required, outgassing rates play a major role.

To systematically study their outgassing rates, different metals, polymers and ceramics were investigated at the Outgassing Measurement Apparatus (OMA) at KIT. OMA uses the so-called difference method, a modified throughput method, to determine specific outgassing rates related to the geometrical surface area of the sample. The advantage of the difference method is that a second vacuum chamber, which is identical to the sample chamber, is used as a reference in order to directly subtract the background outgassing rate of the chamber.

The investigated materials include stainless steel 316L, tungsten and copper alloys, Viton® and Vespel® as well as alumina, titanium nitride and silicon carbide, for example.

This paper compares the results of the performed outgassing rate measurements of the different materials as a function of time and temperature, ranging from 10^{-2} to 10^{-9} $\mathrm{Pa{\cdot}m^3/(s{\cdot}m^2)}$. Information about the outgassing species are furthermore determined with a quadrupole mass spectrometer. Finally, the influence of manufacturing and pre-treatments of the samples will be discussed and a recommendation regarding the use of the material in vacuum is given.

VT-Invited On Demand-37 SynRad and MolFlow for Vacuum Analysis of CERN*, **Marton Ady**, R. Kersevan, P. Baehr,* CERN, Switzerland **INVITED**

SynRad+ and MolFlow+ are Monte Carlo simulators for synchrotron radiation (SR) and ultra-high vacuum (UHV), currently developed at CERN.

SynRad+ allows to trace photons - emitted by common magnetic accelerator elements - in a geometry describing the vacuum chamber by polygons. The calculated SR flux can be converted to dynamic gas load, and imported to MolFlow+ for an independent UHV simulation, predicting the pressure profile.

This talk presents recent developments, such as the transition to open-source and cross-platform, the support for geometry editing within the graphical user interface, and an external tool to convert large accelerator sequences to optics and geometry files readable by the codes.

The future development roadmap is outlined, including scripting and iterative simulations. Of particluar importance, the effort to run the codes on latest-generation Nvidia GPUs is presented, with early results showing 300x speedup on entry-level consumer cards. Finally, the feasibility of running the codes on high-performance clusters is discussed.

VT-Invited On Demand-43 Next Generation Synchrotron Light Source: Vacuum System of the 3 GeV Electron Storage Ring at MAX IV Laboratory*, **Marek Grabski**,* Max IV Laboratory, Sweden **INVITED**

The 3 GeV electron storage ring at MAX IV laboratory is the first synchrotron light source that implemented compact multi-bend achromat (MBA) magnet lattice to lower the beam emittance, and fully coated with non-evaporable getter (NEG) vacuum system to ensure low gas density. The storage ring started commissioning in August 2015 and currently delivers photon beams from insertion devices to several beamlines that are in user operation or commissioning.

Several technological challenges had to be tackled in order to achieve ultra-low emittance of the stored electron beam. One of the challenges was the vacuum system, which had to cope with severe space constraints, imposed by the compact MBA lattice, and intense synchrotron radiation from the circulating electron beam. To ensure compact, reliable and cost effective solution the vacuum chambers were constructed out of water cooled, extruded copper pipes. The inner surface of the vacuum system was NEG coated all along the storage ring circumference.

After over 5 years since the start of commissioning, the NEG coated vacuum system proved to be reliable and conditioning well. Average dynamic pressure measured around the storage ring is below 1 picobar and is reducing with the accumulated beam dose. The beam lifetime related to residual gas density is greater than 39 Ah. The total beam lifetime is above the design value of 5 Ah - thus is not limited by the vacuum level. Several successful interventions to install new vacuum components were performed on a few achromats in the storage ring during shutdowns. This was done utilizing venting of the system with purified neon gas, thus avoiding the need of re-activation of the NEG coating and saving intervention time without compromising the storage ring performance.

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

VT-Invited On Demand-49 Vacuum Technology of Hyperloop*, **Tom Kammermeier**,* Leybold GmbH, Germany*; D. Corcoran,* Leybold USA Inc.*; S. Rosenstraeter,* Leybold GmbH, Germany **INVITED**

The anticipated demand of vacuum technology for a large scale Hyperloop track of some hundreds of kilometers is enormous. Even though the requirements of evacuating a huge air-filled chamber and the maintaining of a low pressure environment seems simple at a first glance, the details might be much less trivial. Unlike every other vacuum chamber in the world, in this case, the pumping stations will be scattered over hundreds of kilometers. Pressure variations along the track are only permissible in a small range, otherwise there would be an impact on the pods' aerodynamics. The operation pressure must be a trade-off between aerodynamic friction, energy consumption of the pumping system and a low leak rate of the tube construction. Finally, a short pump down time after e.g. a maintenance interval is desirable but easily impacts the investment into vacuum pumps – and can result in an unnecessary abundance of pumping speed, which could mean a lot of idle machinery during standard operation.

Peak energy consumption for any hyperloop vacuum system will occur during end-to-end pump-down along the track. Pump down times of the order of 12–24 hours can be anticipated. Issues for pump systems can include overheating due to gas compression; overloading of the motors; or exceeding temperature limits due to low heat dissipation at low gas pressures. Total pumping speed requirement can easily add up to millions of m^3/h for a 1000 km track. In view of this, calculations of power requirements or energy consumption, respectively, have become as important as vacuum performance.

By using the Leybold-Simulation Software, we have calculated different scenarios. The software accounts for all relevant parameters like pumping speed curves, conductance effects of piping, energy consumption, variable rotation speeds depending on gas load etc. Results are discussed in particular with regard to energy efficiency.

VT-Invited On Demand-55 Latest Developments and Uses of Neg Technology in Fusion Energy Applications*, **Enrico Maccallini**, P. Manini, M. Urbano, F. Siviero, L. Caruso, A. Ferrara, M. Mura,* SAES Getters SpA, Italy*; M. Siragusa, E. Sartori, P. Sonato,* CONSORZIO RFX, Italy*; G. Motojima, T. Murase, S. Masuzaki, T. Morisaki,* NIFS, Japan*; C. Day, S. Hanke,* KIT, Germany **INVITED**

ZAO® is a new sintered getter material allowing the use of the Non-Evaporable Getter (NEG) technology in fusion energy applications where large fluxes of hydrogen and its isotopes have to be adsorbed/desorbed with unchanged pumping properties over multiple cycles. In this presentation, we report the experimental characterization of ZAO®sintered getters, in pressure regimes and sorption amounts relevant for fusion applications. Experimental results will be presented on the integration of ZAO®based pumping system in final applications such as NBI and divertor devices.

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