

Quantum Science and Technology Mini-Symposium Room B110-112 - Session QS+EM+TF-MoM

Materials for Quantum Computation and Quantum Information

Moderators: Robert Grubbs, IMEC Belgium, Dave Pappas, Rigetti Computing

8:20am QS+EM+TF-MoM-1 High Stability Metal-Based Single Electron Transistors for Silicon Quantum Dot Charge Sensors, Runze Li, University of Maryland College Park; P. Namboodiri, NIST-Gaithersburg; Y. Hong, N. Ebadollahi, University of Maryland College Park; J. Pomeroy, NIST-Gaithersburg

Extremely stable metal-based single electron transistors (SETs) are fabricated using a plasma oxidation technique, resolving the time stability problem that has been a major disadvantage for metal-based SETs. Metal-based SETs were studied extensively ~20 years ago, but were abandoned due to the much worse instability in the charge sensing results compared to Si-based SETs. The most severe instability was a low-frequency noise called "charge offset drift," which causes random and unreproducible readout. Our goal is to produce high stability aluminum-based SETs using plasma oxidation and couple them to Si-based QDs as the charge sensor. The plasma oxidation reduces the two-level defects in the tunnel junction, and we consequently gain a significantly lower charge offset drift of $\Delta Q_0 = 0.13 e \pm 0.01 e$ in 7 days compared to $\Delta Q_0 > 1 e$ in 1 day for thermally oxidized Al-SETs in the literature. However, we are only able to get an output current of ~4 pA during our measurements, which is insufficient as a charge sensor. Our current goal is to increase the output current to ~100 pA (similar to the level of Si-based SETs) by lowering the resistance of the AlOx tunnel junctions. Increasing the tunnel junction area will decrease the resistance, but also increase capacitance, so we are reducing the oxidation time from 7 seconds (which is the oxidation duration for the stabilized SETs being made) to 3 seconds, to reduce the resistance of the tunnel junction by ~10 times.

8:40am QS+EM+TF-MoM-2 High-quality and High Deposition Rate Atomic Layer Deposition of NbN and TiN for Superconducting Quantum Applications, H. Knoops, Oxford Instruments Plasma Technology, Netherlands; L. Bailey, D. Besprozvanny, M. Powell, Oxford Instruments Plasma Technology, UK; Russ Renzas, Oxford Instruments Plasma Technology

Due to the potential of excellent film control, uniformity, and conformality, atomic layer deposition (ALD) is seen as very promising for quantum devices where interface and material quality and their uniformities are a big challenge. Furthermore, for superconducting circuits, the deposition rate of ALD can be an issue, since a high enough film thickness (> 50 nm) is needed to minimize kinetic inductance effects on resonator frequency and where the shielding effectiveness of superconducting vias for crosstalk mitigation depends on film thickness and film conformality in the 3D structures. The challenge here is to deliver sufficiently fast processes while maintaining the desired film properties.

Here, we will share our recent development of a high-quality superconducting NbN and TiN for quantum applications, such as resonators and interconnects, capable of depositing > 50 nm film thickness in two hours. The RF-driven remote plasma source design and chamber of our system is optimized for ALD and allows for deposition rates which are > 3x faster than conventional substrate-biased plasma ALD deposition of similar materials.

The quality of the deposited films was demonstrated to be excellent, as measured by four-point probe electrical resistivity, conformality (100% on 8:1 trench for NbN, verified by SEM), and superconducting transition temperature (T_c). Good superconductive properties of the film were demonstrated by SQUID measurements. Thickness uniformity of < $\pm 5\%$ across a 150 mm Si wafer was achieved with good repeatability. We will also show how stress can be tuned as a function of process parameters, such as the RF source power.

Emerging quantum technologies based on superconducting nitride materials are showing great promise and will benefit not only from the uniformity of the deposition, conformality and film quality, but also from the speed and control provided by this ALD process.

9:00am QS+EM+TF-MoM-3 Navigating MBE Growth of Atomically Precise Complex Oxides using Source Chemistry, Bharat Jalan, University of Minnesota, USA INVITED

From its beginnings as a successful method for III-V semiconductor growth to today for the growth of many contenders for next-generation electronics, spintronics and quantum devices, molecular beam epitaxy (MBE) has been very successful. However, several challenges exist for metal oxide growth where a metal is hard-to-oxidize and/or difficult to evaporate/sublimate. In this talk, I will review these issues and will present my group's effort to address these challenges using a novel solid-source metal-organic MBE approach. We show, for the first time, controlled synthesis of metal and metal oxides of these "stubborn" elements with the **same ease and control** as afforded by III-V MBE. We will present detailed growth study utilizing chemistry of source materials as a controlling knob to navigate synthesis. With the goal to understand and control electronic ground states in defect-managed complex oxide films and nano-membranes, we will discuss how chemistry of source materials can be used to navigate synthesis on-demand.

9:40am QS+EM+TF-MoM-5 Atomic Layer Deposition of Superconducting Titanium Nitride for Through-Silicon-Via Structures and Photon Detection, John Femi-Oyetoro, H. LeDuc, P. Day, M. Dickie, F. Greer, Jet Propulsion Laboratory (NASA/JPL)

Superconducting detectors (SDs) play a crucial role in solving various problems in astronomy and cosmology, including dark matter, exoplanet transit spectroscopy, quantum computing and information. An example of such devices is the microwave kinetic inductance devices (MKIDs). This device has been employed in answering questions about the first light emitted after the big bang approximately 14 billion years ago. SDs make use of thin films of superconducting materials, such as titanium nitride (TiN), because of their high intrinsic kinetic inductance (KI) and large London penetration depth, which makes them particularly interesting and useful. In this study, we demonstrate the atomic layer deposition (ALD) of high-quality TiN with high transition temperature (T_c) and KI suitable for large photon detector arrays and high-density through-silicon-via (TSV) structures. ALD-TiN provides an alternative and reliable source of high-quality films for scarce high-quality sputtering targets. Additionally, these films are expected to be more uniform than reactive sputtered films, which is crucial for cm-scale detector arrays, increasing the absolute detector yield on each wafer. We explored various precursors, gas chemistries, techniques, and deposition conditions, including temperatures as low as 200°C. In particular, we also employed ion bombardment via RF biasing for our deposition process. This is a unique method for removing oxygen impurities, a major contributor to low-quality and high-resistivity films. Furthermore, this energy supply facilitates film densification, efficient elimination of precursor ligand residues, and surface adatom diffusion. We are able to repeatedly deposit a film of ~ 54 nm on a planar 6-inch wafer that transitions and superconducts at $T_c = \sim 4.35$ K. Overall, our goal is to produce SC films with spatial uniformity, highly conformal, and high T_c to overcome the challenges of large detector arrays and interconnect density using 3D integration. The results aiding these efforts will be discussed further.

10:40am QS+EM+TF-MoM-8 Molecular Beam Epitaxy of Superconducting ZrN Thin Films on GaN Substrates, Brelon May, K. Vallejo, D. Hurley, K. Gofryk, Idaho National Laboratory

Group III-Nitride materials have found applications in optoelectronics and photonic devices due to the large variation in direct bandgap spanning from the infrared to the deep ultraviolet. Recent research has pursued the integration of this well-established material system with transition-metal nitrides to create complex heterostructures with additional magnetic or superconducting functionality. ZrN is a well-known refractory conductor with high oxidation resistance, high hardness, and has been shown to be a superconductor at low temperatures. The estimated lattice mismatch of ZrN with InN, GaN, and AlN is 8.5%, -1.5%, and -4.2%, respectively, suggesting strain free as well as strain-tunable growth on the ternary III-Ns. This work focuses on the epitaxial growth of ZrN on c-plane GaN substrates via molecular beam epitaxy. An electron beam evaporation source and an RF-plasma source were used to supply the Zr and active nitrogen, respectively. Reflection high energy electron diffraction (RHEED) and X-ray diffraction (XRD) did not reveal any crystallographic texture of ZrN deposited on fused silica at temperatures >700°C. However, growth of ZrN on c-plane GaN substrates at similar temperatures was epitaxial. RHEED revealed that the ZrN maintains the symmetry of the underlying GaN throughout the entire deposition, and post-growth examination via XRD

showed (111) oriented ZrN thin films. RHEED patterns during the regrowth of GaN directly on thicker layers of higher symmetry ZrN suggest a preference for twin formation and a slight degree of surface faceting. A physical property measurement system was used to measure electrical transport as a function of temperature and magnetic field. Initial results of uncapped ZrN thin films reveal a superconducting phase with a critical temperature of <10 K and a critical field of 2 T. Because the critical temperature is lower than expected, the presence of off stoichiometry or structural disorder is suspected. These results pave the way for integration of superconductors and quantum phenomena in existing III-N photonic systems.

11:00am QS+EM+TF-MoM-9 Enhancing Quantum Circuits Through Biased Plasma-Enhanced ALD of Ultrathin Superconducting TaC_xN_{1-x} *Silke Peeters*, Eindhoven University of Technology, Netherlands; *C. Lennon, V. Seferai, R. Hadfield, M. Weides*, University of Glasgow, UK; *M. Verheijen, E. Kessels*, Eindhoven University of Technology, Netherlands; *H. Knoops*, Eindhoven University of Technology, Oxford Instruments, Netherlands

Superconducting quantum circuits are one of the leading architectures in quantum computing platforms. Recent experiments [1,2] demonstrating up to 0.5 ms coherence time in superconducting Ta transmon qubits mark a six order of magnitude improvement in superconducting qubit coherence over the past two decades [3,4]. However, major material challenges, such as uncontrolled oxides and disordered interfaces, still stand in the way of realizing large-scale, fault-tolerant quantum computers.

In this contribution, material properties of ultrathin TaC_xN_{1-x} are extensively characterized and coupled to cryogenic superconducting quantum device performance. In this way, we aim to clarify the roles of various processing aspects in achieving high-quality-factor devices. TaC_xN_{1-x} films with thicknesses of 7 – 40 nm were prepared by plasma-enhanced atomic layer deposition (PEALD) with radiofrequency substrate bias. Because of its atomic-scale growth control PEALD is a promising technique for growth of thin films with high-quality interfaces. Ion energy control in the ~25 – 250 eV range is provided by the substrate bias.

We have observed that energetic ions can counteract oxygen impurity incorporation and promote a larger grain size, while minimizing ion-induced material damage. Increasing the ion energy from ~25 eV to ~150 eV yields a hundredfold decrease in room-temperature resistivity to 239 μΩ cm for an 18 nm film. Smooth, dense, polycrystalline TaC_xN_{1-x} films of the fcc crystal structure are obtained, which are stable in ambient atmosphere. These films maintain a high critical temperature of superconductivity (T_c) of 7 K down to 11 nm film thickness.

The high ultrathin-film quality achieved by PEALD with substrate bias is promising for ultrathin, low-loss superconducting quantum devices. Specifically, superconducting resonators were fabricated from 20 - 35 nm TaC_xN_{1-x} films on high-quality silicon and sapphire substrates, with preliminary measurements showing internal quality factors of at least 2×10^5 in the single-photon regime. Furthermore, we provide practical pointers for quantum device compatibility of ultrathin superconducting films. Through the high level of control in PEALD with substrate bias, this work contributes to the understanding of material loss mechanisms in superconducting quantum circuits.

References

1. P. M. Place *et al.* Nat. Commun. **12**, 1779 (2021).
2. C. Wang *et al.* npj Quantum Inf. **8**, 3 (2022).
3. W. D. Oliver and P. B. Welander *MRS Bulletin* **38**, 816 (2013).
4. D. Gill and W. M. J. Green *IEEE ISSCC* 30 (2020).

11:20am QS+EM+TF-MoM-10 Characterization of Ultra-Thin Superconducting TaN Nanowires with Integrated Heatsink Capabilities for SNSPD Applications, *Ekta Bhatia*, NY CREATES; *T. Nanayakkara, C. Zhou*, Center for Functional Nanomaterials, Brookhaven National Laboratory; *T. Vo*, American Institute for Manufacturing Integrated Photonics; *W. Collison, S. Schujman, A. Biedron, J. Nalaskowski, S. Olson*, NY CREATES; *S. Kar*, American Institute for Manufacturing Integrated Photonics; *H. Frost*, College of Nanoscale Sci. & Eng., SUNY Polytechnic Institute; *J. Mucci, B. Martinick, I. Wells, T. Murray, C. Johnson, V. Kaushik*, NY CREATES; *C. Black, M. Liu*, Center for Functional Nanomaterials, Brookhaven National Laboratory; *S. Papa Rao*, NY CREATES

Tantalum nitride (TaN) has emerged as a promising candidate for superconducting nanowire single-photon detectors (SNSPD) due to its favorable properties such as lower T_c that enables easier Cooper-pair breaking and a longer wavelength cut-off [1]. TaN is also attractive because it is widely used in the CMOS IC industry enabling TaN SNSPDs to be readily made at a large scale, on 300 mm wafers. While the body of knowledge about superconducting TaN has been growing, its knowledge at 300 mm scale is limited. In this work, we report on the superconducting properties of 300 mm scale TaN and its dependence on process variables. We then discuss the impact of novel integration schemes on the thermal characteristics of TaN nanowires for SNSPD applications.

Copper encapsulated damascene TaN nanowires (with a N/Ta ratio of 0.53 set by room temperature reactive sputtering conditions) have a coherence length of ~8 nm. This is in rough agreement with prior literature on TaN thin films deposited at 750C on sapphire substrates [2]. Extracted values of effective penetration depth, critical magnetic field, and critical current density are reported. We also studied the T_c , I_c dependence on varying thicknesses and line widths (100 nm to 3000 nm). Our TaN nanowires exhibit a T_c of ~3.45 K (at a thickness of ~35 nm) with <5% variation across the 300 mm wafer. Sheet resistance (at 300 K) and I_c vary by < 5% across the 300 mm wafer for all the line widths measured, similar to the < 5% cross-wafer non-uniformity of thickness (XRR) and N/Ta ratio (SIMS & XPS). We also investigated the superconducting properties of different in-film N/Ta ratios varying from 0.35 to 0.7 using 20 nm thick nanowires.

We explored the efficacy of Cu as a heat transport material that is integrated with TaN nanowires in various schemes (damascene Cu above the nanowire, and a blanket underlayer of Cu) and compared to a control case with no Cu. We used the ratio of retrapping current to I_c as the metric of heat transfer efficiency. This study demonstrates a novel way to increase heat transport away from the nanowire, hence improving the reset times of SNSPDs. We discuss one possible design of a focal plane array of fast SNSPDs based on the findings of this work. This study further strengthens the case for scalable fabrication of TaN nanowires using state-of-the-art 300 mm process tools, with applications ranging from arrayed detectors for cosmology to single photon detection in photonic quantum computing and superconducting optoelectronic neuromorphic computing.

[1] A. Engel *et al.* Appl. Phys. Lett. **100**, 062601 (2012).

[2] K. Il'in *et al.* Physica C **470**, 953–956 (2010).

Authors 1 and 2 contributed equally.

11:40am QS+EM+TF-MoM-11 Cryogenic Microwave Loss Measurements of Metal-Oxides using 3D Superconducting Cavities, *Nicholas Materise*, Colorado School of Mines, USA; *J. Pitten*, University of Colorado Boulder; *W. Strickland, J. Shabani*, New York University; *C. McRae*, University of Colorado Boulder/National Institute for Science and Technology (NIST)

Reports of high performance tantalum-based qubits has stimulated interest in comparing the quality of tantalum pentoxide with niobium pentoxide and suboxides of niobium. Here, we present a high participation cavity capable of resolving differences in losses due to oxides grown on Ta and Nb thin films. We distinguish losses of the oxide from the other interfaces using in a multi-step measurement process, first measuring the substrate with its native oxide, then repeating the measurement with the film deposited on the same substrate with oxide grown on the surface. Participation ratio calculations estimate the losses due to each interface, with their thicknesses measured by cross-sectional transmission electron microscopy. This measurement capability opens possibilities to screen candidate materials, and their oxides, for use in superconducting qubits and devices.

Nanoscale Science and Technology Division

Room B113 - Session NS+EM+MN-MoA

Nanoscale Devices, Structures and Materials

Moderators: **Aubrey Hanbicki**, Laboratory for Physical Sciences, **Deep Jariwala**, University of Pennsylvania

1:40pm **NS+EM+MN-MoA-1 Integrated Nanophotonics Temperature Metrology Platform**, **Nikolai N. Klimov**, **K. Douglass**, **D. Barker**, **T. Bui**, **S. Robinson**, **T. Herman**, **K. Quelhas**, National Institute of Standards and Technology (NIST)

Temperature, being, perhaps, the second most measured physical property after time and frequency plays a crucial role in various aspects of modern technology ranging from medicine and Earth's climate to semiconductor industry and advanced manufacturing process control. While there have been great strides in developing novel thermometry approaches, resistance-based thermometry remains the standard method for disseminating the SI unit of temperature at the highest level of precision. The fundamental limitations of resistance thermometry, as well as the desire to reduce sensor ownership cost, have ignited a substantial interest in the development of alternative technologies such as photonics-based temperature sensors.

At the National Institute of Standards and Technology (NIST), we are developing a new photonics-based temperature measurement solution that has the potential to revolutionize how temperature is realized and disseminated to customers. One of the key elements of our Photonic Thermometry program is an ultra-Sensitive Photonic Thermometer (SPoT) – an on-chip integrated silicon nanophotonic resonator, whose optical resonance frequency shifts with temperature due to high thermo-optic coefficient of silicon and can be used to trace temperature variations with high precision. Our goal is to evolve SPoT into a robust, field-deployable device that is on par or better than the state-of-the-art resistance thermometer.

In this work, we describe the performance of SPoT thermometer, as well as a new photonic readout for SPoT. In our new read-out scheme, we employ a novel offset-locking technique for reading out the resonance wavelength of the SPoT. This method provides extremely high accuracy for relative temperature changes on a short time scale ($\ll 1s$). Our results indicated that the packaged on-chip integrated SPoT can detect temperature fluctuations as small 2 μK over 200 ms integration time. This methodology as well as other proposed methods will be discussed. We also show a benchmark comparison of SPoT thermometer to Standard Platinum Resistance Thermometer (SPRT) – the best-in-class resistance thermometer, in various fixed-point cells of ITS-90, evaluating temperature resolution and repeatability

2:00pm **NS+EM+MN-MoA-2 AVS Dorothy M. and Earl S. Hoffman Scholarship Recipient Talk: Breaking the Efficiency Bottleneck of Micro-LEDs Through Nanoscale and Excitonic Engineering**, **Yixin Xiao**¹, **R. maddaka**, **Y. Wu**, **Y. Malholtra**, **Y. Guo**, **S. Yang**, **K. Sun**, **A. Pandey**, **J. Min**, **Z. Mi**, University of Michigan, Ann Arbor

The performance of conventional optoelectronic devices, such as LEDs and laser diodes, is extremely sensitive to the presence of defects and dislocations. For these reasons, it has remained challenging to achieve high efficiency nanoscale LEDs and laser diodes. For example, while conventional broad area LEDs can exhibit external quantum efficiency (EQE) in the range of 80-100%, the EQE of submicron scale LEDs is often $<1\%$, due to the dominant nonradiative surface recombination. The operation of conventional LEDs involves the radiative recombination of free electrons and holes in the active region. It is known that an exciton, a bound state of an electron and hole through strong Coulomb interaction, can drastically enhance the radiative recombination efficiency, which can be potentially exploited to make micro and nanoscale LEDs relatively immune from the presence of defects/traps. Recent studies have shown that the exciton oscillator strength can be increased by nearly two orders of magnitude in small size InGaN nanowires, due to efficient strain relaxation. Here we demonstrate that the efficiency bottleneck of μ LEDs can be fundamentally addressed by utilizing bottom-up III-nitride nanostructures. We report on the demonstration of micrometer scale green and red LEDs with an external quantum efficiency of 25% and 8%, respectively, which are the highest values ever reported to the best of our knowledge. We employ selective

area plasma-assisted molecular beam epitaxy as the material synthesis platform. Due to efficient strain relaxation, such bottom-up nanostructures are largely free of dislocations. By exploiting the large exciton binding energy and oscillator strength of quantum-confined InGaN nanostructures, we show that the external quantum efficiency of a green-emitting micrometer scale LED can be dramatically improved from $\sim 4\%$ to $>25\%$. The dramatically improved efficiency is attributed to the utilization of semipolar planes in strain-relaxed nanostructures to minimize polarization and quantum-confined Stark effect and the formation of nanoscale quantum-confinement to enhance electron-hole wavefunction overlap. We have further developed a new approach that included an InGaN/GaN short period superlattice together with an InGaN quantum dot active region to achieve high efficiency red emission. A maximum quantum efficiency of $>7\%$ was measured. Our studies offer a viable path to achieve high efficiency micrometer scale LEDs for a broad range of applications including mobile displays, virtual/augmented reality, biomedical sensing, and high-speed optical interconnects, that were difficult for conventional quantum well based LEDs.

2:20pm **NS+EM+MN-MoA-3 Modeling Gas Phase Etching in High Aspect Ratio Stacked Nanostructures for Semiconductor Processing: Stacked SiGe Layer Etching**, **Zach Zajo**, Stanford University; **D. Mui**, **J. Zhu**, **M. Kawaguchi**, Lam Research Corp.; **E. Shaafeh**, Stanford University

Gate all around (GAA) nano-transistors offer better channel control and increased current carrying capacity compared to FinFETs (Field Effect Transistor) which are currently the standard in the semiconductor industry. However, the need for precise control of their nanoscale features poses a challenge in manufacturing such GAA nano-transistors. The high material selectivity required in fabricating these transistors makes gas phase etching much more appealing in comparison to liquid phase and plasma-based etching techniques. An etching configuration that is of particular interest is one consisting of alternating layers of Si and SiGe from which the SiGe layers are selectively etched by fluorine gas. In the etching of these structures, it is important to have a uniform etch-rate for SiGe layers from top to bottom, to maintain consistency of the etched features. This consistency is essential for the superior performance of the GAA devices. The key gas phase processing challenge then is to determine and maximize the number of SiGe-Si layers that can be stacked in a single structure while still maintaining a nearly uniform etch-rate from top to bottom in the stack. While experiments have offered insights in terms of the effect of layer thickness, number of layers, gas pressure etc. on the viability of the process, such experiments are quite expensive and tedious. We propose and develop computer simulations as a tool to predict the etch profile evolution over time in a gas phase etching process. The tool is based on a mathematical model which considers the transport processes and surface interactions involved in the gas phase etching process – which at the nanoscale is primarily governed by Knudsen diffusion in the free molecular flow regime. Thus, the transport model is formulated as a boundary integral equation which takes into account the direct flux of etchant molecules that any given point on the exposed surface receives from the bulk gas phase as well as the re-emission flux from other parts of the structure itself. We compared the applicability of two different surface reaction models - a model where the local etch rate is linear in the flux at a point and a Langmuir adsorption/reaction model- to connect the net flux received at a point on the surface to the local etch rate. Our results show that the re-emission of etchants at the etching interface plays a vital role in determining the differential etch rates observed across layers at different depths in the stacked feature. In addition, we have characterized the effect of layer thickness and the spacing between adjacent stacks as these impact the etch rates observed from layer to layer.

2:40pm **NS+EM+MN-MoA-4 Fabrication of Silicon Microfluidic Gratings for Neutron Imaging**, **S. Robinson**, **R. Murphy**, National Institute of Standards and Technology (NIST); **Y. Kim**, National Institute of Standards and Technology (NIST)/ University of Maryland, College Park; **J. LaManna**, **C. Wolf**, **K. Weigandt**, **D. Hussey**, **Nikolai N. Klimov**, National Institute of Standards and Technology (NIST)

In this work, we describe the development of a spatial modulator for x-ray and neutron beams. Current technology for x-ray and neutron phase imaging uses individual source gratings with a fixed period to modulate the beams. Each fixed-period, or "static" source grating, has a limited range in spatial resolution at a specific length scale, thus, a relatively larger set of individual static source gratings is required to achieve high-resolution imaging. Our team is developing a neutron imaging technique that will probe heterogeneous samples across multiple length scales. To address the need for a large variability of source grating periods, we are building a

¹ AVS Dorothy M. and Earl S. Hoffman Scholarship Recipient
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silicon microfluidic-based device, DynAmic ReconfigURable Source grating (DARIUS), that itself is capable to adjust, with high resolution, the grating period from 20 μm to 20,000 μm . With such on-demand tunability, a single DARIUS has the potential to replace more than 500 static source gratings, minimizing the need of fabricating, installing, and aligning a new source grating for the required period. To achieve such functionality, DARIUS features over 5,000 microfluidic grating channels that are etched on both the front and back sides of a 100 mm silicon wafer. Each of these grating channels can be selectively infilled with a neutron and/or x-ray absorbing fluid, and provide real-time reconfigurable spatial modulations for neutron and x-ray beams. In this work, we present updates on the double-sided deep silicon etch (on the front and the back of the wafer), as well as the front-to-back alignment of the silicon channels. We also describe the progress towards wafer bonding to seal the front and back sides of DARIUS device. Due to the challenges of both the microfluidic control and tight fabrication tolerances, we are evaluating the design specifics to address larger grating periods.

3:00pm NS+EM+MN-MoA-5 The Small Shift Matters – Submilliradian Tilt Goniometry in Scanning Electron Microscopy, Andrew Madison, J. Villarrubia, D. Westly, R. Dixon, C. Copeland, National Institute of Standards and Technology (NIST); J. Gerling, K. Cochrane, A. Brodie, L. Murray, KLA-Tencor; J. Liddle, S. Stavis, National Institute of Standards and Technology (NIST)

Electron optical aberrations degrade the accuracy and reliability of scanning electron microscopy. Among multiple aberrations of potential concern, an axial tilt of the electron beam shifts the apparent positions and deforms the intensity profiles of features in scanning electron micrographs. Measurement of the beam tilt can enable either a physical correction of beam deflection or an analytical correction in a measurement function. In this study, we report a novel reference structure and image analysis method to measure such shifts, among other key effects. Our new concept has the potential to improve accuracy in scanning electron microscopy, with multifunctional standards enabling integrative calibrations of beam tilt and beyond. Such advances will be of particular interest in semiconductor manufacturing metrology, where even the small shift matters.

We explore conical frustum arrays as multifunctional reference structures, using physical theory to guide ongoing experiments. For a tilt inclination ϑ , a centroid shift s between the top and bottom edges of a conical frustum shows the effect of tilt. For a frustum height h , the measurement function is simply $\vartheta = \sin^{-1}(s/h) \approx s/h$, yielding a null-tilt sensor and self-calibrating goniometer. To understand the limiting random effect of shot noise, we simulate frustum images using a physical model of electron scattering and emission. At a dose of 60 electrons per nm^2 , model shifts show the possibility of submilliradian accuracy for sidewall angles greater than approximately 40 mrad. In experimental measurements, charge accumulation and hydrocarbon contamination may limit the achievable electron dose, while conical asymmetry among other systematic effects will ultimately limit accuracy. In initial experiments, we fabricate submicrometer frustum arrays in silicon using electron-beam lithography and reactive ion etching and demonstrate use of the reference structure in calibrations of a typical scanning electron microscope.

In an integrative calibration, frustum arrays are optimal structures for correlative atomic force, super-resolution optical, and scanning electron microscopy. This workflow yields reference heights and positions that allow calibration of scale factor and correction of scanfield distortion, improving the accuracy of centroid shifts to show electron beam tilt and spatial variation thereof across the imaging field.

4:00pm NS+EM+MN-MoA-8 On Point – Accurate Integration of Quantum Dots and Bullseye Cavities, Craig Copeland, A. Pintar, R. Dixon, A. Chanana, K. Srinivasan, D. Westly, B. Ilic, M. Davanco, S. Stavis, NIST-Gaithersburg

Self-assembled quantum dots are promising light sources for quantum networks and sensors. These emerging technologies require the accurate integration of quantum dots and photonic structures, but epitaxial growth forms quantum dots at random positions in semiconductor substrates. Optical localization of these random positions can guide the placement of photonic structures by electron-beam lithography. This integration process requires the reliable registration of position data across microscopy and lithography systems. However, large errors can result from multiple sources, including lithographic and cryogenic variation of reference dimensions for microscope calibration, as well as localization errors from optical distortion. Such errors tend to increase across an imaging field, presenting a critical impediment to exploiting the throughput and scalability of widefield

microscopy. In this study, we target this problem and show how our solution enables accurate integration to improve device performance and process yield. We develop our methods of traceable localization to calibrate a cryogenic localization microscope – an optical microscope with the sample and objective lens inside of a cryostat, and custom optics outside of the cryostat. We fabricate and characterize arrays of submicrometer pillars in silicon, creating microscopy standards with both traceable reference positions and traceable reference data for thermal expansion coefficient. We image these arrays with the cryogenic microscope at approximately 1.8 K, localize the pillar positions, and use the reference data to calibrate the microscope. Our calibration determines the scale factor of the imaging system and corrects position errors due to complex distortion, among other aberration effects. We combine the results of this cryogenic calibration with our previous assessment of fabrication accuracy by electron-beam lithography, introducing a comprehensive model of the effects of registration errors on Purcell factor. This performance metric quantifies the radiative enhancement that occurs upon integration of a quantum dot into a bullseye resonator. The Purcell factor reaches a maximum value of approximately 11 for error-free registration of the quantum dot and resonator center. Our model demonstrates the possibility of greatly improving Purcell factor across a wide field. Depending on the Purcell factor threshold, on-point integration can increase yield by one to two orders of magnitude. This foundation of accuracy will enable a transition from demonstration devices to efficient processes, leading to the reliable production and statistical characterization of quantum information systems.

4:20pm NS+EM+MN-MoA-9 Nanostructured Gas Sensors for the Detection of Meat Spoilage, Ken Bosnick, National Research Council of Canada

The sustainability of the food industry will remain a key societal challenge in the decades ahead. In North America, over 20% of meat produced is wasted, mostly at the later stages in the supply chain [1]. When meat begins to degrade, it releases biogenic amines (e.g., putrescine, $\text{H}_2\text{N}-(\text{CH}_2)_4-\text{NH}_2$) for which early detection provides a means to sense the onset of spoilage [2]. Early detection of meat spoilage through the sensing of such amines can proactively assure quality in the food production process and potentially eliminate the need for food recalls and other waste. At the heart of these envisioned quality assurance strategies are portable devices that are capable of rapid detection of low levels of biogenic amines and that can be easily deployed at various stages in the production process. New material technologies with a selective response to low levels of biogenic amines are needed to enable these envisioned devices.

The use of MOS-type gas sensing technology represents a promising avenue for portable gas sensors with many advantages over competing sensing technologies and over more traditional analysis methods. We have investigated the application of Pd-decorated ZnO nanoflowers in a chemiresistive sensing mechanism and found an excellent response of 99.5% at 250 $^\circ\text{C}$ towards 400 ppm methylamine [3]. The device also shows a promising response of 45% at room temperature, making it a candidate sensing material for early detection of spoilage in meat-based products. Towards improved performance at room temperature, ZnO nanocantilevers [4] are being investigated for amine sensing and will also be discussed.

[1]FAO. 2011. “Global food losses and food waste – extent, causes and prevention”

[2]Fernanda Galgano, Fabio Favati, Malvina Bonadio, Vitina Lorusso, Patrizia Romano, “Role of biogenic amines as index of freshness in beef meat packed with different biopolymeric materials”, Food Res. Int., 42 (2009) 1147

[3]Jennifer Bruce, Ken Bosnick, Elham Kamali Heidari, “Pd-decorated ZnO nanoflowers as a promising gas sensor for the detection of meat spoilage”, Sens. Actuators B Chem. 355 (2022) 131316

[4]Kissan Mistry, Viet Huong Nguyen, Mohamed Arabi, Khaled H. Ibrahim, Hatameh Asgarimoghaddam, Mustafa Yavuz, David Muñoz-Rojas, Eihab Abdel-Rahman, and Kevin P. Musselman, “Highly Sensitive Self-Actuated Zinc Oxide Resonant Microcantilever Humidity Sensor”, Nano Lett. 22 (2022) 3196

Monday Afternoon, November 6, 2023

4:40pm **NS+EM+MN-MoA-10 From Natural to Fabricated Gas Sensing Photonic Nanostructures: Unexpected Discoveries and Societal Impact, Baokai Cheng, J. Brewer, B. Scherer, R. Potyrailo, GE Research Center**

Existing gas sensors often degrade their performance in complex backgrounds. Thus, new sensing approaches are required with improved sensor selectivity, accuracy, and stability for demanding applications ranging from homeland security, to industrial process monitoring and safety, and to monitoring of outdoor and indoor pollutants and volatile biomarkers.

In this talk, first, we will demonstrate and analyze capabilities of natural photonic nanostructures as sensors for detection of different gases and the origins of these capabilities. Next, we will demonstrate that this new acquired knowledge from studies of natural nanostructures allowed us to develop design rules to fabricate nanostructures for needed gas selectivity and stability for numerous gas monitoring scenarios at room and high temperatures. These design rules for selective gas sensors bring a multivariable perspective for sensing, where selectivity is achieved within a single nanostructured sensing unit, rather than from an array of separate sensors. We fabricated bioinspired nanostructures using several contemporary technologies and have achieved several new functionalities beyond Nature. By utilizing individual nanostructured sensors rather than sensor arrays we also have improved sensor stability by eliminating independent aging factors in separate sensors and their arrays. The use of existing and our new machine learning (a.k.a. multivariate analysis, chemometrics) tools further advanced our sensor designs and performance in detection of multiple gaseous species. The achieved performance capabilities of our developed bio-inspired photonic gas sensors complete with the capabilities of existing commercially available gas sensors and their arrays. These colorimetric sensors can be tuned for numerous gas sensing scenarios in ambient and high temperatures, in confined areas or as individual nodes for distributed monitoring.

5:00pm **NS+EM+MN-MoA-11 Argon-Plasma Dry Etch of sub-Micron Feature-Size Waveguides in Thin-Film Lithium Niobate, Sesha Challa, N. Klimov, P. Kuo, NIST-Gaithersburg**

Lithium Niobate (LN) possesses exceptional properties such as a wide transparency range, large non-linear coefficient, and high-electro-optic efficiency. These properties along with successful implementation of periodic poling in LN have spurred the development of devices finding applications in spectroscopy, remote sensing, and quantum communications.

Despite these valuable properties and possessing large second-order non-linearity, LN has taken a backseat to compete integrated photonic platforms, such as silicon, which has no second-order nonlinearity. This was due to difficulties in fabrication of a low-loss LN waveguides (WGs), integration, as well as processing on a wafer-scale.

With commercial TFLN wafers now being accessible, in parallel with the rapid advancement of scalable micro-/nano fabrication techniques, TFLN photonic devices are steadily emerging. By offering tighter confinement compared to ion-exchanged WGs, TFLN WGs boost the performance of devices such as EOMs to have bandwidth with smaller power consumption.

Etching LN is however challenging, hence, making it difficult to fabricate low-loss WGs. In particular poor etch induces substantial roughness and non-vertical side-wall angles contributing to high propagation losses in the WGs. Low-loss LN WGs have been demonstrated over the past several years. Most of these WGs were fabricated using argon gas inductively coupled reactive ion plasma (ICP-RIE) etching. Etch recipe optimization is of utmost importance to reduce optical losses. Initial demonstrations have shown that TFLN devices can match or exceed the performance of traditional silicon or indium phosphide devices. However, low-loss TFLN waveguides are not widely available.

As a part of the effort to develop low-loss TFLN devices, we perform a systematic study of fabrication high-quality LN WGs. The main goal of this investigation is to reduce the WG's surface roughness while keeping an optimum side-wall angle profile that minimizes light propagation loss. In particular, our efforts are focused on three criteria: (1) selecting appropriate mask materials to reduce the transfer of mask defects into LN WGs, (2) establishing the optimal plasma chemistry by detailed study of various ICP-RIE etch parameters, and, (3) determining the optimum chemical cleaning protocol to remove the redeposited during ICP-RIE etch material on the WG's side-wall. In this presentation, we discuss the details of all three fabrication aspects to make high-quality TFLN devices and structures.

Atomic Scale Processing Mini-Symposium Room A107-109 - Session AP+EM+PS+TF-TuM

Area Selective Processing and Patterning

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

8:00am **AP+EM+PS+TF-TuM-1 Area-Selective Deposition in Nanoscale Patterns, Annelies Delabie**, Imec Belgium, and KU Leuven Belgium; *J. Clerix*, IMEC Belgium; *K. Van Dongen*, IMEC, Belgium; *J. Sinha*, IMEC Belgium; *L. Myns*, IMEC, Belgium; *R. Nye*, LAM Research; *G. Parsons*, North Carolina State University; *J. Swerts*, IMEC Belgium

INVITED

Manufacturing nano-electronic devices becomes more and more complex as the device dimensions reach the nanoscale and a wide range of new materials is being implemented to achieve high device performance. Additional complexity comes from the use of three dimensional (3D) structures to reduce the active footprint. Area-Selective Deposition (ASD) provides a promising avenue to assist and/or even simplify device manufacturing processes. ASD is a technique to deposit material only on a pre-defined area of a patterned surface (the growth area), while no deposition is intended on other areas of the same surface (the non-growth area). As such, ASD can be used to replicate patterns on 3D substrates and to (partly) fill narrow trenches or holes from the bottom up. ASD can be achieved by tuning the adsorption and diffusion kinetics in atomic layer deposition (ALD) and chemical vapor deposition (CVD) processes. Insight in the chemical and physical processes is essential to enable rational design of new ASD processes for nano-electronic device manufacturing for advanced technology nodes.

This presentation will discuss the growth mechanisms during ASD on substrates that contain nanoscale patterns, where the geometry of the nanopatterns can affect the growth behavior, selectivity and uniformity. An aminosilane small molecule inhibitor can enable ASD on a wide range of materials with SiO₂ as the non-growth surface [1]. The selectivity of TiO₂ ALD relies mainly on adsorption. Selectivity loss during TiO₂ALD occurs via a nucleation site generation mechanism: small TiO₂ nanoparticles are continuously generated during ALD by slow, unintentional adsorption on the passivated non-growth surface area [2]. ASD super cycles consisting of inhibitor adsorption, TiO₂ ALD and etch effectively improve the selectivity, but may compromise the height uniformity in nanoscale patterns. The selectivity of Ru and Ge₂Sb₂Te₅ ALD relies on a complex interplay of adsorption, diffusion and aggregation. We reveal a pattern-dependent selectivity for Ru ALD, which is explained by aggregation of Ru adspecies at the pattern edges [3]. We conclude that the selectivity and uniformity of ALD processes can change when pattern dimensions reach the nanoscale.

[1] K. Van Dongen et al, *J. Vac. Sci. Technol. A* 2023, 41, 032404.

[2] R. A. Nye et al, *Appl. Phys. Lett.* 2022, 121, 082102.

[3] J.-W. J. Clerix et al, *Appl. Surf. Sci.* 2023, 626, 157222.

8:40am **AP+EM+PS+TF-TuM-3 N-Heterocyclic Carbenes as Small Molecule Inhibitors in AS-ALD, Cathleen Crudden**, Queen's University, Canada

INVITED

A unique carbon-based SMI, called an N-heterocyclic carbene (NHC), has been developed as a small molecule inhibitor using carbon as the heteroatom. NHCs have been used in organometallic and catalysis chemistry for decades, where they are renowned for their ability to form strong bonds to metal surfaces. We have developed a suite of organic SMIs with high volatility and thermal stability enabling deposition in an ALD tool. We demonstrated strong binding of the SMI to Ru, Co, Mo and Cu and selectivity for binding to metal surfaces in the presence of insulators. These results are informed by surface science studies including microscopy and spectroscopy.

9:20am **AP+EM+PS+TF-TuM-5 Unraveling Precursor Blocking Mechanisms in Area-Selective Atomic Layer Deposition Using Small Molecule Inhibitors, Olaf Bolkenbaas, M. Merckx**, Eindhoven University of Technology, Netherlands; *P. Yu*, Eindhoven University of Technology, Netherlands; *T. Sandoval*, Universidad Tecnica Federico Santa Maria, Chile; *E. Kessels*, A. Mackus, Eindhoven University of Technology, Netherlands

Area-selective atomic layer deposition (ALD) has garnered significant attention as a potential technique for enabling the further miniaturization of semiconductor devices. One method for achieving area-selective ALD is through the use of small molecule inhibitors (SMIs) that selectively block deposition on certain materials. Previous research has indicated that

precursor blocking by SMIs involves two components: the chemical removal of reactive surface sites and the physical blocking of the surface, also referred to as chemical passivation and steric shielding respectively [1]. However, it is difficult to differentiate between these two factors as they occur simultaneously. In this work we attempt to unravel the steric shielding and the chemical passivation contributions by the SMI acetylacetone (Hacac) with the use of reflection adsorption infra-red spectroscopy (RAIRS) on dehydroxylated Al₂O₃ surfaces obtained through annealing.

When comparing Hacac adsorption on an as-prepared and an annealed Al₂O₃ surface using RAIRS, a lower amount of Hacac adsorbates was observed on the annealed surface. Furthermore, a higher fraction of the Hacac adsorbates was present in the more strongly bonded chelate configuration. This difference in the distribution of the binding configurations demonstrates that the density of surface sites affects the SMI adsorption behavior. We expect that this different adsorption behavior is caused by a lower amount of steric hindrance between the SMIs on the annealed Al₂O₃ surface. Furthermore, the increase in the amount of adsorbates in the chelate configuration will result in a higher contribution of chemical passivation on the dehydroxylated surface, since only the adsorbates in the chelate configuration chemically passivate the surface [2]. From this we can conclude that the removal of surface sites can be used to obtain a better understanding of the two precursor blocking mechanisms. This better understanding will create opportunities for the development of new area-selective ALD strategies involving the removal of reactive surface sites before the functionalization with SMIs to improve selectivity.

[1] Merckx, et al., *Chem. Mater.* **32**, 3335–3345 (2020).

[2] Mameli et al., *ACS Nano* **11**, 9303–9311 (2017).

9:40am **AP+EM+PS+TF-TuM-6 Topographically-Selective Deposition Using Amorphous Carbon as Inhibition Layer, Thijs Janssen, M. Merckx, W. Kessels, A. Mackus**, Eindhoven University of Technology, The Netherlands

To accommodate the increasing complexity of device architectures in nanoelectronics, new nanoscale processing techniques are required. Selective deposition techniques have been developed in recent years to enable bottom-up and self-aligned processing^{1,2}. While traditional area-selective deposition distinguishes between areas depending on their chemical character, topographically-selective deposition (TSD) distinguishes between areas based on their orientation within a 3D structure^{2,3}. Such TSD approaches offer new fabrication opportunities, for example when the growth and non-growth areas possess similar material properties, or when too many different materials are present within the device structure. Previously reported TSD methods have been demonstrated only for specific materials.

In our work, we develop a versatile TSD strategy that is potentially suitable for a broad range of materials. Our approach utilizes a pulsed Ar/CH₄ plasma to selectively apply an amorphous carbon (aC) inhibition layer on horizontally-oriented surfaces by relying on the directional ions from the plasma. The vapor-phase selective deposition of aC is integrated together with existing ALD processes and plasma treatments into a TSD supercycle recipe.

The highly inert surface of aC lacks suitable absorption sites for ALD precursors and co-reactants, making it an effective inhibition layer. It was found that only the horizontally-oriented surfaces are covered by the aC layer, thus subsequent ALD of target materials proceeds exclusively on vertically-oriented surfaces.

Successful ALD inhibition on the aC surface is established for several different target materials such as TiO₂ using TDMAT and H₂O, Nb₂O₅ using TBTDEN and H₂O, and NiO_x using Ni(BuAMD)₂ and H₂O. In particular 90% selectivity was maintained for 35 cycles TiO₂ deposition (1.09 ± 0.01 nm selective growth), 70 cycles Nb₂O₅ deposition (4.38 ± 0.02 nm) and 40 cycles of NiO_x deposition (1.28 ± 0.01 nm). It is demonstrated for NiO_x that the supercycle can be repeated, which effectively resets the nucleation delay, such that a thicker film (nominally ~5 nm after 4 supercycles) can be deposited selectively.

1. Mackus, A. J. M., Merckx, M. J. M. & Kessels, W. M. M. From the Bottom-Up: Toward Area-Selective Atomic Layer Deposition with High Selectivity. *Chem. Mater.* **31**, 2–12 (2019).
2. Parsons, G. N. & Clark, R. D. Area-Selective Deposition: Fundamentals, Applications, and Future Outlook. *Chem. Mater.* **32**, 4920–4953 (2020).

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3. Chaker, A. *et al.* Topographically selective deposition. *Appl. Phys. Lett.* **114**, (2019).

11:00am **AP+EM+PS+TF-TuM-10 A ReaxFF Study for Hacac Interaction on Al₂O₃ Surface in Area-Selective ALD, Naoya Uene**, Tohoku University, Japan; *I. Tezsevin, W. Kessels, A. Mackus*, Eindhoven University of Technology, Netherlands; *A. van Duin*, Pennsylvania State University; *T. Tokumasu*, Tohoku University, Japan

An area-selective ALD process of SiO₂ was developed comprising acetylacetone inhibitor (Hacac), bis(diethylamino)silane precursor (BDEAS), and O₂ plasma reactant pulses. Hacac inhibitors lead to delayed SiO₂ growth on the Al₂O₃ surface for about 15 ALD cycles, after which the selectivity is lost. Two chemisorption configurations of Hacac inhibitors on Al₂O₃ surfaces have been reported: monodentate and chelate configurations. (Merx *et al.* 2020) Density functional theory (DFT) calculations have shown that the monodentate configuration is relatively reactive with incoming BDEAS, causing the loss of selectivity due to precursor-inhibitor reactions. Therefore, exploration of the relative densities of the chelate/monodentate configurations on the surface is crucial for the understanding of the selectivity loss mechanism. We aim to understand the reaction mechanisms of Hacac inhibitor adsorption on Al₂O₃ surfaces at the atomic scale.

Up to now, the investigation of the adsorption of inhibitor molecules has been studied via DFT calculations. Thereactive force-field molecular dynamics (ReaxFF MD), which can simulate chemical reactions and physical dynamics at the atomic scale, has been used for gas-surface systems. (van Duin *et al.* 2001) We performed ReaxFF MD simulations to consider the chemical reactions of Hacac inhibitor molecules with dislocation effects on the surface. An initial force field has been developed for the Hacac interaction on Al₂O₃ surface based on the two existing force fields: Li/Si/Al/O force field for Al₂O₃ structure and protein force field for carbohydrate interactions. (Kim *et al.* 2016; Monti *et al.* 2013) The initial force field is trained for Hacac geometry, and their reaction on an OH-terminated Al₂O₃ surface is also modeled.

We performed ReaxFF MD simulations using the developed force field. The simulation consists of three steps. First, the Al₂O₃ surface is pre-thermally relaxed. Then, the Hacac inhibitor is supplied on the relaxed surface, followed by post-thermal relaxation of the Hacac-adsorbed surface. We first confirmed the temperature stability of the Al₂O₃ surface with different temperatures. Our force field can control the temperature of the Al₂O₃ surface ranging from 300 K to 1500 K. Next, sequential adsorption of 20 Hacac inhibitor molecules was simulated on the temperature-controlled Al₂O₃ surface, as shown in the supplemental document. The findings from our ReaxFF simulations provide in-depth insights into the mechanisms of Hacac adsorption and saturation on the surface. These insights will be used for the investigation of precursor blocking and blocking selectivity loss in our future work.

11:20am **AP+EM+PS+TF-TuM-11 Enhancement of TMSDMA Passivation on SiO₂ by Surface Fluorination, Anthony Valenti**, SUNY College of Nanoscale Science and Engineering; *C. Vallée*, SUNY College of Nanoscale Science and Engineering, France; *C. Ventrice*, SUNY College of Nanoscale Science and Engineering; *K. Tapily, K. Yu, S. Consiglio, C. Wajda, R. Clark, G. Leusink*, TEL Technology Center, America, LLC, USA

With the ever-shrinking scale of semiconductor devices, area-selective atomic layer deposition (AS-ALD), a bottom-up and self-aligned patterning process with atomic-scale control has been in development in order to meet the demands of industry. This technique is typically conducted by promoting growth on specific surface termination types, while inhibiting growth on the other surface types of the substrate via selective chemisorption of molecules that are inert to the deposition process. With its affinity for chemisorbing to hydroxylated oxide surfaces, specifically SiO₂, but not on Si or non-oxidized metal surfaces, N-(trimethylsilyl)dimethylamine (TMSDMA) has been of recent interest for its use as a small molecule inhibitor (SMI) for area selective deposition (ASD). Upon interaction with a surface hydroxyl group, the TMSDMA molecule dissociates, resulting in a trimethylsilyl group bonded to the chemisorbed oxygen atom of the hydroxyl group. Although TMSDMA-passivated SiO₂ typically remains inert over several ALD cycles, nucleation of the growth precursor can eventually occur. This may be due to hydroxyl groups on the surface that did not interact with TMSDMA molecules and/or non-hydroxylated sites that were not passivated by trimethylsilyl groups. For instance, surface siloxane bridges do not dissociate TMSDMA and can act as nucleation sites for the ALD growth precursor. In order to enhance the passivation of SiO₂ surfaces, the use of co-passivants has been explored. In

particular, a remote NF₃ plasma has been studied as a means for forming a co-inhibitor. Dosing before or after TMSDMA treatment has been investigated. The deposition of the small molecules were carried out on 10 Å SiO₂/Si(100) substrates. Water contact angle measurements were taken to determine relative surface passivation of each sample. Angle-resolved X-ray photoelectron spectroscopy and attenuated total reflection/Fourier transform infrared spectroscopy were performed in order to characterize the chemical state of each surface. Our results indicate that exposure of the substrate to the NF₃ plasma after passivation with TMSDMA, results in damage to the passivating layer. However, exposure of the surface to the NF₃ plasma before TMSDMA exposure maintains the passivation of the SiO₂ surface. In addition, temperature programmed desorption (TPD) measurements are being conducted to assess the relative coverage of the inhibiting film on each sample and its thermal stability.

11:40am **AP+EM+PS+TF-TuM-12 A Study of Elucidation and Improvement of TiO₂ Selectivity by First-Principles Based Thermodynamic Simulation, Yukio Kaneda**, Sony Semiconductor Solutions Corporation, Japan; *E. Marques, S. Armini, A. Delabie, M. van Setten, G. Pourtois*, IMEC, Belgium
INVITED

Area-selective deposition (ASD) enables the deposition of materials in a targeted area, typically a pre-patterned surface, while preventing the growth on adjacent surfaces.[1] The technique is appealing for both academia and industry as it offers a vehicle to simplify material developments in nanoelectronics. Consequently, numerous efforts have been dedicated to investigate the factors driving the selectivity mechanisms and to identify optimal process deposition conditions, including surface treatments, that enable highly selective processes.

The “selectivity” dimension results from the identification of the right combination of precursors (including co-agents), surface treatments, and reactor operating conditions. This is typically a complex and laborious process that requires many systematic and tightly controlled experiments. As a result, the development of highly selective ASD processes is often a slow and challenging task where any form of guidance provided by modeling insights can be precious.

In this context, we studied, by combining thermodynamic considerations and first principle simulations, the reactivities of complex surface chemical reaction networks and the factors impacting on selectivity. In this talk, we will discuss the case of the ASD of TiO₂ on SiO₂ substrates terminated with either “reactive” (-OH) or “passivated” alkyl-silyl groups. First, we will first briefly discuss the validation of our approach by comparing our model prediction with experimental measurements for the case of the ALD of TiO₂ using the precursors TiCl₄ and Ti(OMe)₄ and then report the insights gained for the identification of optimum Ti precursor and inhibitor for the ASD of TiO₂. We will then extend the discussion to the case of the ASD supercycles of TiO₂, where the interaction of some Ti precursors (or of their ligands) leads to the degradation of the surface “passivation” and then requires restoring the surface by injecting of alkyl-silyl functional groups. We will review the strategies that worked with their drawbacks.

[1] Gregory N. Parsons and Robert D. Clark, *Chem. Mater.* **2020**, 32, 12, 4920–4953

[2] Job Soethoudt, *et al.*, *The Journal of Physical Chemistry C* **2020** *124* (13), 7163-7173

[3] Janne-Petteri Niemelä *et al.*, *Semicond. Sci. Technol.* **2017** 9 (32), 093005

Nanoscale Science and Technology Division Room B113 - Session NS+2D+EM+MN+SS-TuM

Scanning Probe Microscopy

Moderators: Aubrey Hanbicki, Laboratory for Physical Sciences, **Fernando Castro**, National Physical Laboratory, U.K.

8:00am **NS+2D+EM+MN+SS-TuM-1 AVS Medard W. Welch Award Talk: Microscopy is All You Need: The Rise of Autonomous Science, Sergej Kalinin**¹, University of Tennessee Knoxville
INVITED

Making microscopes automated and autonomous is a North Star goal for areas ranging from physics and chemistry to biology and materials science – with the dream applications of discovering structure-property relationships,

¹ Medard W. Welch Award Winner

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exploring physics of nanoscale systems, and building matter on nanometer and atomic scales. Over the last several years, increasing attention has been attracted to the use of AI interacting with physical system as a part of active learning – including materials discovery and optimization, chemical synthesis, and physical measurements. For these active learning problems, microscopy arguably represents an ideal model application combining aspects of materials discovery via observation and spectroscopy, physical learning with relatively shallow priors and small number of exogenous variables, and synthesis via controlled interventions. I introduce the concept of the reward-driven experimental workflow planning and discuss how these workflows can be implemented via domain-specific hyper languages. The applications of classical deep learning methods in streaming image analysis are strongly affected by the out of distribution drift effects, and the approaches to minimize though are discussed. The real-time image analysis allows spectroscopic experiments at the predefined features of interest and atomic manipulation and modification with preset policies. I further illustrate ML methods for autonomous discovery, where the microstructural elements maximizing physical response of interest are discovered. Complementarily, I illustrate the development of the autonomous physical discovery in microscopy via the combination of the structured Gaussian process and reinforcement learning, the approach we refer to as hypothesis learning. Here, this approach is used to learn the domain growth laws on a fully autonomous microscope. The future potential of Bayesian active learning for autonomous microscopes is discussed. These concepts and methods can be extended from microscopy to other areas of automated experiment.

8:40am **NS+2D+EM+MN+SS-TuM-3 Dielectric Constant Measurement Sensitivity in Electrostatic Force and Force Gradient Microscopy-Based Modes**, *Gheorghe Stan*, National Institute of Standards and Technology (NIST); *C. Ciobanu*, Colorado School of Mines

Understanding of the nanoscale electrostatic interaction between a conductive atomic force microscopy (AFM) probe and a dielectric film is central to the operation of various nanoscale dielectric microscopies and determination of dielectric properties of the film. There is no simple analytical description of the electrostatic interaction generated in the confined probe-sample geometry of neither the static nor dynamic AFM modes used for dielectric measurements. An accurate description of the involved physics is obtained only by means of a finite element analysis modeling of the system. However, the alternative of using numerical analysis is not very popular being slower and requiring relatively high computation resources. In this work we revised the contributions from different parts of the AFM probe to the probe-sample capacitance by both analytical and numerical methods. We tried to reconcile the two approaches and observed the differences as a function of geometry and material parameters. Under various noise levels, the efficiency of an analytical model was tested against finite element analysis that captures in detail the electrostatic interaction in AFM-based dielectric measurements. The investigation was performed in both spectroscopic force-distance curves and constant height scans with measurements for the deflection and frequency of the AFM probe. The obtained measurement sensitivities are relevant in selecting the optimal scanning mode and its operational parameters for given film thicknesses and dielectric constants but are also showing the critical role of the numerical analysis to the correct interpretation of the measurements.

9:00am **NS+2D+EM+MN+SS-TuM-4 Measuring and Understanding the Nanomechanical Properties of Halide Perovskites and Their Correlation to Structure**, *I. Rosenhek-Goldian*, Dept. of Chemical Research Support, Weizmann Inst. of Science, Israel; *I. Buchine*, *N. Prathibha Jasti*, Bar-Ilan Inst. for Adv. Mater. and Nanotechnol. & Dept. of Chem. Bar-Ilan Univ., Israel; *D. Ceratti*, Dept. of Mol. Chem. & Materials Science, Weizmann Inst. of Science, Israel & CNRS, UMR 9006, IPVF, Institut Photovoltaïque d'Île-de-France; *S. Kumar*, Bar-Ilan Inst. for Adv. Mater. and Nanotechnol. & Dept. of Chem. Bar-Ilan Univ. Ramat Gan Israel. & Dept. of Mol. Chem. & Materials Science, Weizmann Inst. of Science, Israel; *D. Cahen*, Bar-Ilan Inst. for Adv. Mater. and Nanotechnol. & Dept. of Chem. Bar-Ilan Univ. & Dept. of Mol. Chem. & Materials Science, Weizmann Inst. of Science, Israel; *Sidney R. Cohen*, Dept. of Chemical Research Support, Weizmann Inst. of Science., Israel

Halide perovskites, HaP, and especially Pb-based ones exhibit a plethora of remarkable properties. Of these, their photovoltaic properties are the most widely studied due to the proven potential these materials hold for significant technological impact. In addition to photoresponse, this material class is characterized by interesting physical properties, of which mechanical properties enjoy special attention, not only because of

potential use in flexible devices, but also from a fundamental science point of view. The mechanical response can shed light on the materials' behavior including dynamic processes and strain-related effects on optoelectronic behavior.

In the context of these studies, particular emphasis has been placed on environmental factors which can alter, especially degrade, material functionality and device performance. Exposure to humidity, light, and oxygen rank prominently amongst these factors.

In this study we measure the humidity influence on the mechanical properties, i.e., elastic modulus (E) and hardness (H), for two series of lead halide perovskite single crystals, varying either by cation or by anion type. Our conclusions are based on comparing results obtained from several different nano-indentation techniques, which separate surface modulus from that of the bulk, and probe different manifestations of the hardness. These studies reveal the different crystalline parameters governing influence of humidity on the mechanics at the surface and in the bulk.

An atypical inverse correlation between E and H was measured (as seen in the supplementary figure a). Furthermore, humidity influenced these two properties in opposite fashion – humidity exposure led to lower H, but to higher E (supplementary figure b). This trend is opposite to that found in most materials where hydration lowers both E and H. We suggest a link between dynamic disorder, self-healing, and the intriguing relation between E and H.

9:20am **NS+2D+EM+MN+SS-TuM-5 3D Nanoprinting of Advanced AFM Nano-Probes**, *Harald Plank*, *M. Brugger-Hatzl*, *R. Winkler*, *L. Seewald*, Graz University of Technology, Austria

The demand for correlative microscopy is still increasing, as it enables a superior ensemble of information by using various methods to combine individual strengths. The highest level of that approach are hybrid microscopes, which enable individual characterization at the very same spot in a consecutive or even parallel way. With that, however, comes the demand of a conflict-free integration of different microscopes, which require a radical redesign of the instrumentation. A major step in that direction is a recently introduced dual system called FUSIONScope, which is a deeply integrated scanning electron microscopy (SEM) and atomic force microscopy (AFM) solution. While the former enables high-resolution guidance towards the region of interest, the latter complements SEM capabilities by true quantitative 3D surface information, which together exploit their full potential by the possibility to precisely land the AFM tip on highly exposed regions. Even more importantly, advanced AFM modes such as conductive AFM (CAFM), magnetic force microscopy (MFM), electrostatic / Kelvin force microscopy (EFM/KFM), scanning thermal microscopy (SThM) or mechanical mapping, provide functional information beyond SEM capabilities. For that, special nano-probes are required, which typically achieve their intended functionality by additional thin film coatings, which contains two main disadvantages. First, they increase the apex radii and limit the lateral resolution, which is in conflict with the still decreasing feature sizes. Secondly, coatings are prone to delamination during operation, which affects resolution, lateral correlation and reliability. Therefore, to exploit the full potential of advanced AFM modes, it is of great interest to develop new approaches for the fabrication of functional nano-probes. Following that motivation, we joined forces with industry and apply the additive direct-write technology focused electron beam induced deposition (FEBID) for the development of novel 3D nano-probe concepts with industrial relevance. In this contribution, we briefly discuss the 3D nano-printing process and then go through a variety of advanced, FEBID-based tip concepts for CAFM, EFM, MFM and SThM. The joint element for all probes is the coating-free character, which eliminates the aforementioned risks during operation. Additionally, the apex regions are routinely in the sub-10 nm regime, which allows for high-resolution imaging. Aside of comparisons to traditionally used nano-probes, which reveal the superior performance of FEBID-based nano-tips, we discuss on currently ongoing research towards multi-functional AFM tips, based on FEBIDs flexibility.

11:00am **NS+2D+EM+MN+SS-TuM-10 Chemical, Mechanical, and Morphological Evolution of Nanostructures on the Surfaces of Asphalt Binders**, *L. Lyu*, *J. Pei*, Chang'an University, China; *E. Fini*, Arizona State University; *L. Poulikakos*, EMPA (Swiss Federal Laboratories for Materials Science and Technology), Switzerland; *Nancy Burnham*, Worcester Polytechnic Institute

Bitumen (asphalt binder) holds roads together. It is a complex, dynamic, nanostructured material that comes from the bottom of an oil refinery stack—a non-renewable resource. It ages, and it ages more quickly under

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the influence of heat and light. Can additives made from waste materials increase the longevity of bitumen, and thus roads?

In this study, atomic force microscopy (topography, phase imaging, PF-QNM) and its combination with infrared spectroscopy (AFM-IR) were used to explore the chemical, mechanical, and morphological evolution of the surface of bitumen without and with additives. Aging is assumed to begin at the surface.

Samples of bitumen were made with and without introducing bio-modified rubber additives. Each sample was exposed to several thermal and UV aging protocols. Evolution of surface under aging was studied. Depending on the additive and type of aging (thermal, UV, or combined), the nanostructures changed their chemistry, mechanical properties, and size. Furthermore, the matrices and phases immediately surrounding the nanostructures evolved differently upon aging than the included nanodomains. In general, carbonyl and sulfoxide IR bands became more prevalent, the samples became stiffer and less adhesive, and the phase immediately surrounding the nanostructures became smaller. One additive made from two different waste materials was found to enhance the stability of the surfaces.

By understanding the evolution of asphalt binders and which additives promote their stability, longer lasting roads might be designed and built, thereby lowering the need for a non-renewable resource.

11:20am NS+2D+EM+MN+SS-TuM-11 Identifying Potential Carbon Sources for Direct Carbon Material Production by AI Assisted HR-AFM, Percy Zahl, Brookhaven National Laboratory; Y. Zhang, ExxonMobil Technology and Engineering Company; S. Arias, Brookhaven National Laboratory

High-resolution Atomic Force Microscopy (HR-AFM) has proven to be a valuable and uniquely advantageous tool for studying complex mixtures such as petroleum, biofuels/chemicals, and environmental or extraterrestrial samples. However, the full potential of these challenging and time-consuming experiments has not yet been fully realized. To overcome these bottlenecks and enable further research into solutions for the energy transition and environmental sustainability, automated HR-AFM in conjunction with machine learning and artificial intelligence will be crucial [1].

In this study, we focus on identifying potential carbon sources suitable for more direct carbon material production by analyzing various pitch fractions based on their solubility in toluene. Specifically, we present the first comprehensive AI-assisted study of hydrocarbon fractions derived from petroleum and coal tar pitch, using and refining our previously introduced "Automated HR-AFM" tools. We explored four classes derived from Petroleum Pitch (PP) and Coal Pitch Tar (CPT), separated into toluene soluble (TS) and toluene insoluble (TI) fractions. Our analysis revealed differences in the structural characteristics of the molecules, which we binned based on the number of aromatic rings.

(Please see also the in our supplemental document included figures 1 and 2)

Overall, our results demonstrate the potential of automated HR-AFM and AI-assisted analysis for understanding complex mixtures and identifying potential carbon sources for direct carbon material production. This work represents an important step towards more sustainable and environmentally-friendly energy solutions.

Reference:

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11:40am NS+2D+EM+MN+SS-TuM-12 Automated Microscopy for Physics Discovery: From High-Throughput to Hypothesis Learning-Driven Experimentation, Yongtao Liu, R. Vasudevan, M. Ziatdinov, S. Kalinin, Oak Ridge National Laboratory

In this work, we explore the ferroelectric polarization switching in relation to the applied pulse bias including bias voltage and time in scanning probe microscopy (SPM). We perform two types of automated and autonomous experiments. First, we conduct automated high-throughput experimentation to gain a comprehensive understanding of the relationship between pulse biases and ferroelectric domain growth. Second, we employ an autonomous experimentation driven by machine learning (ML) algorithm to optimize experimental conditions based on real-time experiment results.

SPM has proven to be a powerful tool for manipulating and visualizing ferroelectric domains at the nanoscale. Investigations of ferroelectric domain size and stability can advance our knowledge of ferroelectrics application in memory devices, such as operating time, retention time, and

bit size. However, conventional SPM measurements have been time-intensive and dependent on experienced researchers to perform repetitive tasks and make real-time decisions regarding measurement parameters. For example, researchers determine and manually tune the parameters for next iteration of experiment according to the previous results. Here, we perform automated and autonomous experiments in SPM to explore the mechanism of ferroelectric polarization. The first experiment is a high-throughput experiment of applying various bias pulse conditions to write ferroelectric domains followed by imaging domain structure using piezoresponse force microscopy. In this automated experiment, we systematically adapt the bias pulse parameters to gain a comprehensive understanding of their relationship with the resulting domain structures. We discovered different polarization states that show up upon different bias conditions. In the second experiment, we implement a hypothesis active learning (HypoAL) algorithm based on structured Gaussian process to control the SPM for ferroelectric domain writing. The HypoAL analyzes the relationship between the bias pulse conditions and the written domain size in real-time experiments, and determines the bias pulse parameters for the next iteration. The goal of HypoAL is to establish the best physical hypothesis for the material's behaviour within the smallest number of experiment step. The HypoAL identifies that the domain growth in a BaTiO₃ film is governed by kinetic control. The approaches developed here have the potential to be extended to other experiments beyond SPM in the future to accelerate the discovery of new materials and advances in physics.

Quantum Science and Technology Mini-Symposium Room B110-112 - Session QS+EM-TuM

SiC, Diamond and Related Materials for Quantum Information Sciences

Moderators: Erin Cleveland, U.S. Naval Research Laboratory, Cheng Gong, University of Maryland

8:40am QS+EM-TuM-3 Topology, Superconductivity and Unconventional Quantum Criticality in Monolayer WTe₂, Sanfeng Wu, Princeton University
INVITED

Quantum critical points associated with quantum phase transitions are highly intriguing states of matter; yet they are difficult to study. An example is the superconductor to insulator or metal transition in two dimensions (2D), a topic that has a long history in condensed matter research, but many problems remain unsolved. In this talk, I will discuss our recent experimental finding of a quantum critical point in monolayer tungsten ditelluride (WTe₂), a unique 2D crystal in which topology, strong correlations and superconductivity all occur in a single material. We directly measure superconducting quantum fluctuations, whose behaviors are so anomalous that an unusual explanation beyond the conventional Landau-Ginzburg-Wilson paradigm is required.

9:20am QS+EM-TuM-5 Robust Cavity Emitter Coupled System Based on Lifetime-Limited Emission in h-BN, Sanchaya Pandit, Department of Mechanical and Material Engineering, University of Nebraska - Lincoln; Y. Wang, Department of Electrical and Computer Engineering, University of Nebraska - Lincoln

In the field of quantum information technology, it is essential to reach a strong coupling regime, where the coupled systems exhibit quantum coherent oscillations. The ability to control the interactions between the single photon emitter and the cavity mode allows for the manipulation of the photon's quantum state, which is crucial for many quantum applications. Quantum emitters based on defect centers in hexagonal boron nitride (h-BN) have emerged as prominent light sources for integrated quantum photonic applications. Especially, the defect centers with single photon emission around 635 nm have been demonstrated to exhibit lifetime-limited linewidth even at room temperature. This work explores the monolithic integration of this type of h-BN emitters with the whispering gallery mode (WGM) in the microdisk cavity. By optimizing the cavity design, strong coupling between the emitter and cavity has been predicted analytically. Furthermore, coherent manipulation of photon based on cavity-emitter detuning, and spatial position of emitter has been explored and visualized as vacuum Rabi splitting and Rabi oscillation through the Quantum toolbox in Python (Qutip) simulation. The robust cavity design and methodology developed will provide valuable guidelines for the realization of scalable and integrated quantum photonic circuits based on h-BN defect centers.

Tuesday Morning, November 7, 2023

11:00am **QS+EM-TuM-10 Collective Excitations in Topological Materials,**
Stephanie Law, Pennsylvania State University **INVITED**

Topological insulators (TIs) are materials that have a bulk band gap crossed by surface states with linear dispersion. These surface states are present at the physical boundaries of the material, and host two-dimensional, massless electrons that are spin-momentum locked. When they couple to a photon, these electrons form the basis of Dirac plasmon polaritons (DPPs) with resonances in the THz spectral range.

In this talk, I will first discuss our efforts to grow TI materials by molecular beam epitaxy (MBE). The TI materials of interest are Bi₂Se₃, Bi_xSb_{1-x}, and MnBi₂Se₄. These are all two-dimensional materials, meaning that they exhibit a layered structure with van der Waals (vdW) bonding between each layer. Due to the relatively weak interlayer bonding, these materials grow by van der Waals epitaxy, which has unique opportunities and challenges. I will show our results on growing these materials on passivated substrates (e.g. Al₂O₃) and unpassivated substrates (e.g. GaAs and Si).

I will then discuss our efforts to excite plasmonic excitations in these materials. The frequencies of the DPPs are predicted to depend both on the wavevector of the excitation as well as on the film thickness when the film is much thinner than the wavelength of light. In this regime, a DPP is excited on the top surface and on the bottom surface of the film simultaneously. These excitations couple, leading to an acoustic and an optical mode. By mapping this relationship, we have shown conclusively that we are able to excite DPPs in TI thin films. These resonances have mode indices of a few hundred, much higher than what is observed in traditional plasmonic systems, implying that light is strongly confined in these materials. We attribute the large mode index to the fact that we are exciting a coupled optical mode and that the bulk permittivity of the TI is also large. Unlike most materials, the large mode index does not lead to a decrease in lifetime. Instead, the lifetime of the mode determined by the full width at half maximum is a few hundred femtoseconds. We attribute this relatively long lifetime to the spin-momentum locking of the surface state electrons, which reduces their probability of scattering. We have also demonstrated coupling of the DPPs in the plane using a stripe array as well as coupling out of plane by growing a layered structure. Finally, we have created a multilayer structure comprising alternating layers of a TI and a normal insulator, leading to a Dirac hyperbolic metamaterial in the THz.

11:40am **QS+EM-TuM-12 Novel Particles in 2D Materials Detected with Quantum Interference and Raman,** **Kenneth Burch**, Boston College **INVITED**

The pursuit of new quasi-particles is driven by the quest to uncover novel phases of matter, emergent phenomena. These may also serve as a foundation for future technological innovations. In this presentation, I will elaborate on our utilization of Raman spectroscopy to identify emergent particles in 2D materials. Firstly, I will delve into our endeavors to identify fractional spin excitations in RuCl₃. Subsequently, I will highlight our recent breakthrough in discovering the Axial Higgs mode, which results from Quantum Geometry and a charge density wave. This discovery was facilitated by Raman's unique ability to detect the particle's symmetry and employ quantum interference to unveil its Axial properties.

Atomic Scale Processing Mini-Symposium

Room A107-109 - Session AP1+2D+EM+PS+TF-TuA

Atomic Layer Processing: Integration of Deposition and Etching

Moderator: John F. Conley, Jr., Oregon State University

2:20pm **AP1+2D+EM+PS+TF-TuA-1 Combination of Plasma-Based Atomic-Scale Deposition and Etching Processes for Advanced Patterning**, **Marceline Bonvalot**, LTM - MINATEC - CEA/LETI, France; **C. Vallée**, SUNY College of Nanoscale Science and Engineering; **r. gassilloud**, **T. Chevolleau**, CEA/LETI-University Grenoble Alpes, France; **N. Possémé**, STmicroelectronics, France **INVITED**

Selective Deposition processes have gained increased research interest in recent years, because they enable the accurate placement of a thin film on a specific substrate surface (in the case of area selective deposition ASD) or on specifically oriented surfaces (in the case of topographical selective deposition TSD). Such processes require atomic-scale precision, and usually involve Atomic Layer Deposition techniques, with possibly plasma assistance. Several pathways have been proposed in the literature for ASD, most commonly implying surface inhibition treatments with dedicated chemical treatments (self-assembled molecules or small molecule inhibitors for instance) to increase the nucleation delay during the subsequent ALD growth. However, the dedicated inhibition behavior eventually deteriorates when exposed to a few ALD cycles, which requires that on the one hand, nuclei formed on non-growth surfaces be removed and on the other hand, the inhibitor be systematically regenerated.

In this presentation, we will show how the insertion of an *in situ* etching step in the overall ALD process can serve as an effective corrective treatment for this purpose. The etching periodicity in conventional deposition/etching duty cycles will be investigated in details. We will show that the etching step should preferentially be carried out before the transition from the Volmer-Weber 1D island growth mode to the 2D layer by layer growth mode on non-growth surfaces, to limit plasma-induced surface defects. Moreover, the 1D island growth mode seems to coincide with the onset of degradation for the surface inhibition treatment. In this context, it will be shown that the etching periodicity is a determining parameter for the successful development of a selective bottom-up growth strategy.

3:00pm **AP1+2D+EM+PS+TF-TuA-3 Application of Etching Reaction Models to Deposition Processes**, **Nobuyuki Kuboi**, Sony Semiconductor Solutions Corporation, Japan **INVITED**

Advanced CMOS devices require highly intricate 3D stacked structures with varying aspect ratios such as FinFETs and GAAs [1]. Understanding the process properties of plasma etching [2] and deposition [3] processes based on their mechanism and combinations has become increasingly important in addressing this challenge. Additionally, microfabrication properties should be stably suppressed within a specific range during mass production. However, the monitoring system equipped in the process chamber is limited for mass production. Therefore, we propose predictive models for plasma etching and deposition that consider the physical and chemical aspects of the plasma and surface.

First, we briefly introduce simulations for fluctuations in the SiN etching rate influenced by the chamber wall condition, critical dimensions during Si gate etching caused by SiBr_x by-products dependent on open area ratios on wafer/chip/local-pattern levels, damage distribution affected by local-pattern structure, ion energy, and hydrogen concentration in the SiO₂ and SiN films, and selectivity during SiO₂-ALE [4][5][6].

We then present a modeling and simulation of the deposition process as a motif of the SiN-PECVD process using a 3D voxel method that can be associated with the previous process, such as plasma etching [7]. The model can predict film properties as well as the coverage on a large-scale pattern. Reactions among voxels are considered pseudo treatments for atomistic interactions on the surface. A statistical ensemble method involving probabilities is used to express physical and chemical phenomena such as sticking, migration, and bond formation on the deposited surface. The sticking and bond probabilities are affected by surface damage and IEADFs, respectively. Our model can successfully reproduce the experimental characteristic relationship between the morphology and film density dependent on the SiH₄ flow rate during the low temperature (120 °C) SiN-PECVD process considering different gas residence times that affect

surface reactions. Furthermore, we discuss the issue of modeling the ALD process.

These simulation technologies can aid in optimizing the chamber wall condition, pattern design, and etching/deposition combination process.

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4:20pm **AP1+2D+EM+PS+TF-TuA-7 Recent Advancements for Atomic Layer Advanced Manufacturing Processes: Microreactor Direct Atomic Layer Processing (μDALP™)**, **Maksym Plakhotnyuk**, **A. Varga**, **I. Kundrata**, ATLANT 3D Nanosystems, Denmark; **J. Bachmann**, ATLANT 3D Nanosystems; Friedrich-Alexander Universität Erlangen-Nürnberg, Denmark **INVITED**

As the demand for miniaturized and complex devices continues to grow across various industries, the need for innovative and precise atomic layer advanced manufacturing (ALAM) technologies becomes increasingly apparent^[1]. Our company, utilizing proprietary Microreactor Direct Atomic Layer Processing (μDALP™), is at the forefront of pushing sALD's capabilities and broadening its application horizons. The μDALP™ process undergoes the same cyclic ALD process but only in a spatially localized area.^[2] The microreactor or micronozzle confines the flows of gases used for ALD within a defined μm-scale centric area on the substrate to deposit the desired material.^[3]

ATLANT 3D's recent advancements in our novel μDALP™ technology have enabled innovation within the thin film deposition field ranging from ALD material development to rapid prototyping and manufacturing. The μDALP™ process enables multiple depositions e.g., depositions with varying film thicknesses, to be deposited onto a single wafer used to calculate a given processes growth rate within only a few hours, compared to days for a traditional ALD process. In Addition, innovation of applications including optics and photonics, quantum devices, MEMS, RF electronics, emerging memory technologies, advanced packaging, and energy storage are possible and have been demonstrated using μDALP™ technology.

Discussing the improvements to the μDALP™ process, we have decreased the process resolution, increased material compatibility, and accessible morphologies. Giving one example of the recent development in morphologies, films deposited with μDALP™ have conformal coverage of gratings, microchannels, and trenches up to a depth of 25 μm using a Platinum deposition process. **Fig. 1** demonstrates how a given ALD material process (in this case, Pt) can be used with ATLANT 3D technology to deposit localized area conformal coatings of complex surfaces with an aspect ratio of 1:25. Hence demonstrating the versatility and potential of our technology for achieving inherently selective ALD for processing on complex surface morphologies.

This talk aims to shed light on how our breakthroughs in spatial ALD and μDALP™ technology contribute to the advancement of ALAM and scale-up. Fostering a deeper understanding of our technology's capabilities and exploring the possibilities it opens up for various industries.

[1] Poodt P., *JVSTA.*, **2012**, *30*, 010802

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[3] Plakhotnyuk M, *et al.*, *ALD/ALE 2022 [Int. Conf.]*, **2022**

Tuesday Afternoon, November 7, 2023

Biomaterial Interfaces Division

Room B117-119 - Session BI+AS+EM+NS+SE+TF-TuA

Functional Biomaterials II: Sensing and Diagnostics

Moderators: Joe Baio, Oregon State University, Caitlin Howell, University of Maine

2:20pm **BI+AS+EM+NS+SE+TF-TuA-1 AVS Nellie Yeoh Whetten Awardee Talk: Detection of SARS-CoV-2 using Surface-enhanced Raman Spectroscopy and Deep Learning Algorithms, Yanjun Yang¹**, University of Georgia; H. Li, Chongqing University, China; L. Jones, J. Murray, D. Luo, X. Chen, H. Naikare, Y. Mosley, R. Tripp, University of Georgia; B. Ai, Chongqing University, China; Y. Zhao, University of Georgia

A rapid and cost-effective method to detect the infection of SARS-CoV-2 is crucial in the fight against COVID-19 pandemic. This study presents three strategies to detect SARS-CoV-2 from human nasopharyngeal swab (HNS) specimens using a surface-enhanced Raman spectroscopy (SERS) sensor with deep learning algorithms. The first strategy is to use DNA probes modified silver nanorod array (AgNR) substrate to capture SARS-CoV-2 RNA. SERS spectra of HNS specimens have been collected after RNA hybridization, and a recurrent neural network (RNN)-based deep learning (DL) model is developed to classify positive and negative specimens. The overall classification accuracy was determined to be 98.9%. For the blind test of 72 specimens, the RNN model gave 97.2% accuracy in the prediction of the positive specimens, and 100% accuracy for the negative specimens. The second strategy is to use a human angiotensin-converting enzyme 2 protein (ACE2) functionalized SERS sensor to capture the intact viruses. Such a method can differentiate different virus variants, including SARS-CoV-2, SARS-CoV-2 B1, and CoV-NL63. A convolutional neural network (CNN) deep learning model for classification and regression has been developed to simultaneously classify and quantify the coronavirus variants based on SERS spectra, achieving a differentiation accuracy of > 99%. Finally, a direct SARS-CoV-2 detection on SiO₂ coated AgNR substrate is tested. SERS spectra of HNS specimens from 120 positive and 120 negative specimens are collected. The HNS specimens can be accurately distinguished as positive or negative with an overall 98.5% accuracy using an RNN-based deep learning model, and the corresponding Ct value can be predicted accurately by a subsequent RNN regression model. In addition, 99.04% accuracy is achieved for blind SARS-CoV-2 diagnosis for 104 clinical specimens. All the detections are accomplished in 25 min. These results indicate that the SERS sensors combined with appropriate DL algorithms could serve as a potential rapid and reliable point-of-care virus infection diagnostic platform.

2:40pm **BI+AS+EM+NS+SE+TF-TuA-2 Wafer-Scale Metallic Nanotube Arrays: Fabrication and Application, Jinn P. Chu**, National Taiwan University of Science and Technology, Taiwan

This presentation reports on the wafer-scale fabrication of metallic nanotube arrays (MeNTAs) with highly ordered periodicity. Various metals and alloys have been used to prepare MeNTAs via sputtering over a contact-hole array template created in the photoresist. We have used ferrous (stainless steel) and nonferrous (Cu-, Ni-, Al-, and Ti-based) alloys, as well as elemental metals (Cu, Ag, and Au), to form MeNTAs. The proposed nanotubes can be fabricated over a wide range of heights and diameters (from a few hundred nm to 20 μm) in various shapes, including tall cylinders and dishes. In addition, after combining with other nanomaterials (e.g., ZnO nanowires, graphene oxide, or Au nanoparticles), MeNTAs become nanohybrids suitable for many applications. These applications include thermal emitters, triboelectric nanogenerators, SERS-active biosensors, microfluidics, and anti-icing devices.

3:00pm **BI+AS+EM+NS+SE+TF-TuA-3 Low-Cost, Continuous Spectroscopic Monitoring of Chemical and Biological Contamination in Liquids, Liza White, C. Howell**, University of Maine

Traditional UV-visible spectroscopic testing of liquids to assess contamination typically involves manual collection and measurement in a dedicated instrument at discrete time intervals. Here, we describe how low-cost, mass-produced diffraction gratings can be used to approach the functionality of traditional UV-visible spectroscopic readouts under continuous flow conditions. We designed and built a flow chamber setup that permitted uninterrupted monitoring of the diffraction pattern as water with different contaminants was passed over it. Various chemical dyes as well as biological contaminants such as bacteria and algae at varying concentrations in water were tested using standard LEDs as a light source.

Information was extracted from the diffraction patterns by analyzing changes in the transmitted wavelengths as well as changes in scattering. Our results showed that the system permitted reasonable detection of each of the contaminants tested within a subset of the concentration range of a standard UV-vis instrument. Tests using the toxic dye methylene blue showed accurate detection well below the toxic limit (5 μg/mL), although the limit of detection for *E. coli* was higher at ~10⁷ cells/mL. Our results demonstrate how mass-produced diffraction gratings can be used as low-cost detection systems for the continuous detection of contamination in liquids, opening the door for autonomous monitoring for a range of different applications.

3:20pm **BI+AS+EM+NS+SE+TF-TuA-4 Clickable Cerium Oxide Nanoparticles with Gadolinium Integration for Multimodal Micro- and Macroscopic Targeted Biomedical Imaging, Anna du Rietz, C. Brommesson, K. Roberg, Z. Hu, K. Uvdal**, Linköping University, Sweden

Multimodal and easily modified nanoparticles enable targeted biomedical imaging at both the macro- and micro level. Computed tomography and magnetic resonance imaging are biomedical imaging techniques used daily in clinical practice all over the world. These non-invasive techniques can identify more medical conditions if contrast and sensitivity are increased. Commonly, targeted imaging is realized by conjugating biomolecular recognition elements such as antibodies to the contrast agent.

Herein, we present a clickable nanoparticle of our own design, consisting of a Cerium oxide nanoparticle core with integrated Gadolinium, coated with polyacrylic acid and functionalized with both a clickable moiety and a fluorophore. Click chemistry is a versatile toolbox of conjugation reactions that can be performed under gentle conditions enabling facile tailoring of the nanoparticles. Results from XRD and TEM studies clearly show that the cores are mono-crystalline and approximately 2 nm in diameter, the hydrodynamic radius of <5 nm is measured by DLS. The soft coat of the nanoparticles is characterized by IR spectroscopy as well as zeta potential measurements. We have verified the presence of azide-groups on the finished particles and the carboxylic groups of polyacrylic acid are firmly bound to the nanoparticle core. The nanoparticles have high colloidal stability even in physiological ionic strength environments with a zeta potential of -48 mV. We have proven direct anchoring of monoclonal antibody cetuximab to the nanoparticles enabling targeting of epidermal growth factor receptor, a common target in many cancer types. Fluorescence spectroscopy and relaxivity measurements were used to evaluate and optimize the properties for future imaging applications of tumors. The nanoparticles provide high MRI contrast with a T₁ relaxivity of 42 s⁻¹mM⁻¹ Gd, more than two times higher than currently used contrast agents. The finished antibody functionalized nanoparticles are efficiently purified using size exclusion chromatography, separating them from unbound nanoparticles and antibodies. Finally, the cellular uptake of the nanoparticles was evaluated using fluorescence microscopy as well as live/dead assays. We show that the nanoparticles are taken up by cell lines of head- and neck squamous cell carcinoma, in a lysosomal pattern. The nanoparticles are visualized at the nm scale inside the lysosomes using TEM. In conclusion, we have designed and synthesized a versatile nanoparticle with functionalized capping that enables facile fabrication of tailored nanoprobe for biomedical imaging.

4:20pm **BI+AS+EM+NS+SE+TF-TuA-7 Molecularly Imprinted Polymers (MIPs): Rising and Versatile Key Elements in Bioanalytics, J. Völkle, A. Feldner**, Center for Electrochemical Surface Technology, Wiener Neustadt, Austria; P. Lieberzeit, University of Vienna, Faculty for Chemistry, Department of Physical Chemistry, Vienna, Austria; Philipp Fruhmann, Center for Electrochemical Surface Technology, Wiener Neustadt, Austria

INVITED

Molecularly imprinted polymers (MIPs) are specific materials with tailored binding cavities complementary to a specific target molecule. Although the first example of artificial materials with molecular recognition were already described 80 years ago, they experienced a surge of popularity since the late 1990s due to improved synthetic methods and their great potential as recognition element in (biomimetic) sensors. MIPs can achieve similar selectivity and sensitivity as antibodies¹, while their robustness and stability is superior compared to biomolecules. They can also be used under non-physiological conditions, are suitable for long-term storage and accessed by scalable synthetic methods. These properties make them highly promising candidates for a wide range of applications, from biomimetic receptor layers to nanomaterials or artificial antibodies.

¹ AVS Nellie Yeoh Whetten Awardee

Tuesday Afternoon, November 7, 2023

Despite this versatility, their design and optimization towards a specific analyte is probably the most challenging task in the development of a sensor. In general, MIP based sensors either rely on electrochemical, mass sensitive or optical transducers and are commonly used as thin film or nanoparticle (nanoMIP). While there is a considerable amount of literature on electrochemical sensors with MIPs available, new developments such as the improvement of conductive MIPs², optimized epitope imprinting³, or the development of novel synthetic techniques such as the solid-phase synthesis of nanoMIPs⁴ are highly important for the further development of MIPs in sensing.

For this reason, this presentation will provide an overview about different MIP types, their synthesis, application, and challenges. Furthermore, their potential in future applications will be addressed to give a wholistic impression of the numerous possibilities of this versatile compound class.

References

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#equal contribution

5:00pm **BI+AS+EM+NS+SE+TF-TuA-9 X-ray Fluorescence Analysis of Metal Containing Cytostatics in HeLa Cells using the Ultra-compact Cryo-vacuum Chamber μ -HORST, Lejla Jusufagic, C. Rumancev, A. Rosenhahn, A. Steinbrück, N. Metzler-Nolte, Ruhr-University Bochum, Germany**

Synchrotron-based X-ray fluorescence spectroscopy (XRF) is an excellent method for investigating elemental distributions and metal concentrations in biological systems.^[1-4] The method provides a high sensitivity down to the detection of trace elements with high spatial resolution and penetration depth.^[3,4] We introduced an ultra-compact cryogenic vacuum chamber called " μ -HORST" at the P06 nanoprobe beamline at PETRA III, DESY to measure 2D-XRF elemental distribution maps and concentrations in cryogenically fixated cells treated with cytostatic metal complexes with varying ligand sphere.^[1,2] The cells are grown on silicon nitride membranes and treated with a 10 μ M solution of the metal complexes for different durations and all physiological processes were stopped by rapid cryo-fixation. Cryogenic fixation is a non-destructive method that keeps the cells as close as possible to their biologically hydrated state. The frozen cell samples can be transferred into the μ -HORST setup and maintained in a frozen state throughout the nano-XRF measurements. The acquired data show that the concentration of the metal complexes and their intracellular location can be correlated to the one of physiologically relevant ions such as potassium and zinc as well as associated changes in the metal homeostasis. The developed chamber can not only be used for the analysis of intracellular cytostatic metal complexes, but also to the accumulation of antimicrobial metal complexes or of anthropogenic metals in environmental samples.

References

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5:20pm **BI+AS+EM+NS+SE+TF-TuA-10 Hemocompatibility Analysis of Novel Bioinspired Coating, AnneMarie Hasbrook, R. Faase, M. Hummel, J. Baio, Oregon State University**

Surface-induced thrombosis is a critical concern in medical device development. To minimize thrombosis, current extracorporeal circulation units require systemic anticoagulation. However, systemic anticoagulants can cause adverse effects such as thrombocytopenia, hypertriglyceridemia, and hyperkalemia. To address this issue, we combine the technology of polydopamine (PDA) functionalization with slippery liquid infused porous surfaces (SLIPS) to potentially enhance the biocompatibility of medical devices. PDA readily coats a wide variety of surfaces and can be functionalized with a thiolated fluoropolymer, via Michael Addition, to form a pseudo self-assembled monolayer (pSAM) which serves as the porous surface component of SLIPS. Liquid perfluorodecalin can then be added to complete the SLIPS coating. We hypothesized that the PDA SLIPS coating provides enhanced hemocompatibility due to its omniphobic properties and composition of compounds currently used in medical applications. Surface modifications were confirmed using contact angle and X-ray photoelectron spectroscopy (XPS) which revealed significant changes to the surface chemistry after the addition of each subsequent layer of PDA SLIPS. The coatings were evaluated for thrombogenicity via quantification of Factor XII (FXII) activation under static and dynamic settings, fibrin formation, platelet adhesion, and clot morphology. The PDA SLIPS coating activated 50% less FXII than glass and 100% more FXII than bovine serum albumin (BSA) coated substrates. PDA SLIPS had similar plasma clotting time to BSA and plasma clotted two times slower on PDA SLIPS than on glass. Platelet adhesion was increased two-fold on SLIPS compared to BSA and decreased two-fold on SLIPS compared to glass. PDA SLIPS had approximately 20% higher fiber diameter and 25% lower clot density than glass and was significantly different in fiber diameter and density than BSA.

5:40pm **BI+AS+EM+NS+SE+TF-TuA-11 Signal Enhancement for Gravimetric Biomimetic Detection – Conjugation of Molecularly Imprinted Polymer Nanoparticles to Metal Nanoparticles, Julia Völkle, CEST GmbH, University of Vienna, Austria; A. Weiß, P. Lieberzeit, University of Vienna, Austria; P. Fruhmann, CEST GmbH, Austria**

Over the past decades, the field of biosensors and -diagnostics has been increasingly dominated by a growing demand for non-centralized point-of-care devices that do not rely on extensive laboratory infrastructure and trained personnel. Recently, the COVID-19 pandemic has emphasized the crucial role of such fast, reliable, and affordable diagnostic tools. Novel, tailor-made nanomaterials are considered a key component for tackling the upcoming challenges of miniaturization and cost-efficiency in the field of biosensing.

One emerging class of such biomimetic nanomaterials are molecularly imprinted polymer nanoparticles (nanoMIPs). nanoMIPs are artificial receptors that can mimic the highly selective binding capabilities of biological recognition units, such as antibodies and enzymes. Unlike their natural counterparts however, they are stable under a wide range of non-physiological conditions, suitable for long-term storage, and can be derived from a straightforward, rapid synthesis procedure without the need for cell culturing or animal experimentation. Thus, they are ideal candidates for the development of sensitive, robust and inexpensive bioanalogous sensors.

While impressive results regarding their high selectivity and low non-specific binding have been reported [1], nanoMIP-based gravimetric (quartz crystal microbalance, QCM) assays are restricted with regards to the achievable limit of detection by their comparatively low overall mass. This project therefore is focused on the synthesis of well-defined nanoMIP-metal nanoparticle (NP) conjugates, which would result in a larger change in mass upon binding of the recognition units to the QCM transducer. Moreover, conjugation to gold-NPs would allow the incorporation of nanoMIPs into other analytical techniques such as lateral flow devices (LFDs). Experiments therefore are focused on the incorporation of suitable functional groups for further conjugation into the nanoMIP polymer network, the surface functionalization of metal NPs with complementary linker moieties and a suitable coupling procedure. In the poster, nanoMIPs selective for various biologically relevant species are coupled to metal NPs and the performance of the conjugates in QCM-based detection is presented in detail and discussed.

[1] Park, et al. „Recent Advances of Point-of-Care Devices Integrated with Molecularly Imprinted Polymers-Based Biosensors: From Biomolecule Sensing Design to Intraoral Fluid Testing“. *Biosensors* 12, Nr. 3 (22. Februar 2022): 136. <https://doi.org/10.3390/bios12030136>.

Tuesday Afternoon, November 7, 2023

Nanoscale Science and Technology Division

Room B113 - Session NS1+2D+EM+MN-TuA

Nanofabrication and Characterization of Low-Dimensional Materials

Moderator: Georg Fantner, EPFL

2:20pm NS1+2D+EM+MN-TuA-1 Atomic-Scale Design and Defect Networks at the 2D/3D Interface, *Kate Reidy*, MIT INVITED

'Mixed dimensional' 2D/3D van der Waals heterostructures, where 3D metallic nanostructures are integrated with suspended two-dimensional (2D) van der Waals materials, show unique functionalities including light-matter coupling, charge transfer, and enhanced catalytic activity. To enable such integration, an understanding of how structure and defects at the 2D/3D interface affect heterostructure properties is required. Moreover, 2D/3D heterostructures display fluctuations of opto-electronic properties in nanometer spatial range; and it is advantageous to probe position-dependent properties at the same spatial scales. In this seminar, I will share work exploring the local properties of the 2D/3D interface using a combination of atomic resolution scanning transmission electron microscopy (STEM), in situ ultra-high vacuum (UHV) TEM, and monochromated high-energy resolution electron energy-loss spectroscopy (EELS). We demonstrate epitaxial, single-crystalline metallic nanoisland growth of technologically relevant metals (Au, Ti and Nb) with with ultra-low defect density interfaces and faceted morphologies on several thin suspended 2D materials. We then explore the key parameters of 2D/3D growth, including the role of temperature, defects, moiré, surface chemistry, and thermodynamic equilibrium shapes. Lastly, we fabricate more complex heterostructure stacks with defect densities controlled by the compliance of the 2D material substrate. Through fundamental understanding of the structure-property-performance relationship, we suggest that future electronic, magnetic, and optical nanodevices will utilize versatile fabrication of 2D/3D heterostructures with well-characterized interfaces and morphologies.

3:00pm NS1+2D+EM+MN-TuA-3 Highly Asymmetric Doping of Epitaxial Bilayer Graphene by Targeted Bonding of the Intercalated Gadolinium, *Marek Kolmer*, Ames National Laboratory; *J. Hall*, Ames National Laboratory and Department of Physics and Astronomy, Iowa State University; *S. Chen*, *M. Tringides*, Ames National Laboratory, Department of Physics and Astronomy, Iowa State University

Heterostructures consisting of vertically stacked two-dimensional (2D) materials have recently gained large attention due to their highly controllable electronic properties. Particularly, mechanically stacked multilayered systems offer exceptional control over a stacking sequence or interlayer twist angles. On the other hand, epitaxially grown 2D materials express unprecedented quality and stability over wafer-scale lengths. In both cases controlling the interlayer coupling can generate novel electronic and topological phases and its effective implementation is commonly done with a transverse electric field. However, phases generated by high displacement fields are elusive.

Here, we introduce an exceptionally large displacement field by structural modification of a model system: AB-stacked epitaxial bilayer graphene (BLG) on a SiC(0001) surface. We show that upon intercalation of gadolinium with two specific interlayer locations, electronic states in the top two graphene layers exhibit a significant difference in the on-site potential energy (~1 eV), which effectively breaks the interlayer coupling between them. As a result, for energies close to the corresponding Dirac points, the BLG system behaves like two electronically isolated single graphene layers. We prove this fact by a comprehensive multi-technique methodology based on low-temperature scanning tunneling microscopy/spectroscopy (STM/S) and angle-resolved photoelectron spectroscopy, which are corroborated by density functional theory, tight binding, surface diffraction and multiprobe STM transport. The work presents charge transfer from intercalated metal atoms as a promising approach for the synthesis of 2D graphene heterostructures with electronic phases generated by giant displacement fields.

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[2]M. Kolmer, W. Ko, J. Hall, S. Chen, J. Zhang, H. Zhao, L. Ke, C.-Z. Wang, A.-P. Li, M.C. Tringides, "Breaking of Inversion Symmetry and Interlayer Electronic Coupling in Bilayer Graphene Heterostructure by Structural Implementation of High Electric Displacement Fields", *J. Phys. Chem. Lett.* 13, 11571 (2022). <https://doi.org/10.1021/acs.jpclett.2c02407>.

4:20pm NS1+2D+EM+MN-TuA-7 AVS Dorothy M. and Earl S. Hoffman Scholarship Recipient Talk: Exfoliated 2D Nanosheets for Large-Area, Solution-Processed Optoelectronics, *Lidia Kuo*¹, *S. Rangnekar*, *V. Sangwan*, *M. Hersam*, Northwestern University

Two-dimensional (2D) materials exhibit thickness-dependent optoelectronic properties due to their atomically thin nature, unlike their bulk layered crystalline counterparts. In particular, semiconducting MoS₂ undergoes an indirect to direct bandgap transition as the thickness is decreased to the monolayer limit, leading to enhanced optical absorption and emission at the atomically thin scale. Liquid-phase exfoliation (LPE) is a scalable and cost-effective method for obtaining 2D materials from bulk crystals. However, the yield of monolayer sheets by LPE has been impractically low in previous work. The resulting LPE-processed optoelectronic devices have fallen short compared to nanosheets derived from mechanical exfoliation or chemical vapor deposition. Here, we demonstrate that LPE coupled with megasonic exfoliation – i.e., processing at megahertz frequencies compared to the kilohertz frequencies commonly utilized for LPE – yields an unprecedentedly high fraction of monolayer MoS₂. As a result, megasonic exfoliation enables ultrahigh responsivity in printed MoS₂ photodetectors as well as the first demonstration of electroluminescence for large-area, solution-processed MoS₂ films. This work establishes megasonic exfoliation as a scalable and generalizable approach for achieving optoelectronic-grade 2D semiconductors via LPE.

Nanoscale Science and Technology Division

Room B113 - Session NS2+2D+EM-TuA

Light-Matter Interactions at the Nanoscale

Moderator: Nancy Burnham, Worcester Polytechnic Institute

4:40pm NS2+2D+EM-TuA-8 Highly Tunable Room-Temperature Exciton-Polariton Strong Coupling from Monolayer WSe₂ in Nanocavities, *P. Schuck*, *Thomas Darlington*, Columbia University INVITED

In the interaction of light and matter, strong coupling occurs when exchange between a photon and electronic transitions exceeds the relative loss rate leading to hybridization of the optical and electronic states. The behavior is well known in cavity quantum electrodynamics (QED), and is a fundamental ingredient in single photon quantum logic gates. In solid-state systems, many strong coupling phenomena have been explored between different material excitations. Plasmons in particular have attracted great interest owing to their small mode volumes, allowing for strong coupling of a plasmon and single quasi-particles excitations such as excitons, potentially recreating in the solid-state, at the nanoscale, and at elevated temperatures many of the phenomena previously studied in traditional trapped atom QED.

Here, I describe our investigations of strong coupling between TMD excitons and a tunable plasmonic nanocavity formed between a plasmonic tip and gold substrate. Strong coupling between plasmons and excitons has been observed in excitons systems: e.g., J-aggregates, and colloidal quantum-dots. While these systems offer large coupling strengths, the exciton transition energies are largely fixed, and vary randomly depending on variations in growth conditions. By contrast, TMDs offer strong exciton emission and large tunability of exciton energy by applied strain. We utilized this tunability to control coupling strengths in nanocavities in a proof-of-principle nano-electro-mechanical system (NEMS) platform, demonstrating the ability to continuously tune, between weak and strong coupling conditions where we observe both upper and lower polariton bands.

5:20pm NS2+2D+EM-TuA-10 Surface Plasmon Characterization in Ag Nanotriangles for Evaluation of Fano Resonance Conditions, *Nabila Islam*, Department of Physics, Portland State University; *R. Word*, Department of Physics, Portland State University, Portland, Oregon; *E. Abdul*, *S. Rananavare*, Department of Chemistry, Portland State University; *R. Könenkamp*, Department of Physics, Portland State University

Surface plasmon resonances in metal nanostructures allow confinement of the electromagnetic field well below the light diffraction limit and have

¹ AVS Dorothy M. and Earl S. Hoffman Scholarship Recipient

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attracted research interest for a broad range of sensing applications [1]. The comparably broad spectral width of surface plasmon based sensors can be improved by coupling the plasmon resonance to other resonances to generate Fano resonances with the distinctive and sharp asymmetric Fano line-shape. We used photoemission electron microscopy to explore the spectral and spatial behavior of plasmon resonances in structures consisting of a single nanoscale triangular platelet on a substrate providing coupling to a waveguide layer or to an optically active excitonic layer. In our experiments stationary and propagating surface plasmons are optically excited in the nano-triangle at wavelengths around 820-900nm, and multi-photon electron-emission is used to obtain images of the lateral surface plasmon distribution. An aberration-corrected photoemission microscope allowed us to obtain a spatial resolution of ~ 15 nm and a femtosecond pulsed Ti-sapphire laser provided the photon intensities needed for the 3-photon photoemission imaging process [2]. The analysis of the obtained images is done in optical simulations of the same experimental set-up and by calculating the plasmon electric field distribution which is then used to analyze and interpret the photoemission micrographs. The analysis allows to identify the prominent surface plasmon modes and to analyze their interaction to form stationary resonance patterns and propagating modes. Fano-resonances are established in the simulation by placing the triangles in the vicinity of an optical waveguide using an appropriate spacer layer [3]. The simulation then allows to optimize this type of arrangement and to determine locations where the Fano-resonance amplitudes are most pronounced. Simulations of this kind were also applied to the case of gold triangles on substrates provided with exciton and spacer layers. Our results indicate that both the high plasmon field strengths typical for single nanoparticle structures and the sharp spectral features available in Fano-resonances can be combined in these single nano-particle structures, thereby allowing improved resolution in sensor applications.

polarization dependence. We will also discuss how plasmonic heating effects contribute to photocurrent generation. These plasmonic nanogap antennas are subwavelength, tunable photodetectors with sub-bandgap responsivity for a broad spectral range.

References

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259–262. <https://doi.org/10.1016/j.matpr.2022.08.149>

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doi:10.7567/apex.8.022201

5:40pm **NS2+2D+EM-TuA-11 Interconnected Plasmonic Nanogap Antennas for Photodetection via Hot Carrier Injection, John Grasso, R. Raman, B. Willis**, University of Connecticut

Modern integrated circuits have active elements on the order of nanometers; however, optical devices are limited by diffraction effects with dimensions measured in wavelengths. Nanoscale photodetectors capable of converting light into electrical signals are necessary for the miniaturization of optoelectronic applications. Strong coupling of light and free electrons in plasmonic nanostructures efficiently confines light into sub-wavelength volumes with intense local electric fields. Localized electric fields are amplified in nanogap regions between nanostructures where enhancements can reach over 1000. Hot carriers generated within these high field regions from nonradiative decay of surface plasmons can be injected into the conduction band of semiconductors at room temperature, enabling sub-bandgap photodetection. The optical properties of these plasmonic photodetectors can be tuned by modifying antenna materials and geometric parameters like size, thickness, and shape. Electrical interconnects provide connectivity to convert light into electrical signals. In this paper, we will describe the optical properties of plasmonic nanostructures with electrical interconnects and compare experiment and theory using finite-difference time-domain (FDTD) simulations. We will present experimental extinction data and FDTD simulations to elucidate how geometric structure and dielectric properties influence optical properties. We will present sub bandgap photodetection for nanostructures integrated with ALD deposited TiO₂, and investigate both wavelength and

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Applied Surface Science Division

Room B117-119 - Session

AS+2D+CA+EL+EM+MS+NS+SE+SS+TF-WeM

Multi-Modal & Multi-Dimensional Analysis

Moderators: Gustavo Trindade, National Physical Laboratory, UK, Paul Mack, Thermo Fisher Scientific, UK, Tim Nunney, Thermo Fisher Scientific, UK

8:00am AS+2D+CA+EL+EM+MS+NS+SE+SS+TF-WeM-1 **Growth and Characterization of Large-Area 2D Materials**, Glenn Jernigan, US Naval Research Laboratory **INVITED**

Nothing could be more coupled than Growth and Characterization. When two dimensional (2D) materials appeared on the radar of the scientific community (with the amazing properties of graphene), it was immediately obvious that large area samples would be needed. Exfoliating flakes was insufficient for the demands of scientific studies, in addition to not being viable should a commercial application be developed. Thus, the search began for growth methods to produce large-area 2D materials for large scale testing and development.

The Naval Research Laboratory has, over the past 15 years, pursued research programs in producing large areas of graphene, transition metal dichalcogenides (TMDs), boron nitride (BN), and other 2D materials. In every one of those programs, they began with surface analysis of composition, chemistry, and morphology of the grown films. The uniquely sensitive nature of x-ray and ultraviolet photoelectron spectroscopy (XPS and UPS) and scanning tunneling and atomic force microscopy (STM and AFM) to 2D materials was necessary to measure the electrical, chemical, and physical properties obtained in the large area films and to understand what was observed in the exfoliated flakes. The production of large areas allowed "mass-scale" optical and electrical characterization, which then became a feedback loop in the search for new and interesting properties and relevant applications. In this presentation, I will show how we developed large-area graphene, by both epitaxial growth and chemical vapor deposition methods, TMDs, and other 2D materials for characterization and device utilization.

8:40am AS+2D+CA+EL+EM+MS+NS+SE+SS+TF-WeM-3 **Using a Correlative Approach with XPS & SEM to Measure Functionalized Fabrics for Antimicrobial Applications**, Tim Nunney, H. Tseng, Thermo Fisher Scientific, UK; D. Marković, M. Radetić, University of Belgrade, Serbia

Medical textiles are an indispensable component for a wide range of hygienic and healthcare products, such as disposable surgical gowns and masks, or personal protection equipment, with opportunities to provide further protection by engineering textiles with suitable medical finishing. While antibiotics are considered a viable option for their efficiency in treating bacterial infections, their abuse can result in adverse effects, e.g., bacteria resistance. Nanocomposites have emerged as a promising alternative to antibiotics, as the large surface-to-volume ratio and high activity helps attain the targeted antimicrobial efficiency by using tiny amounts of nanocomposites, and their biocompatibility and scalability are particularly advantageous for medical applications [1]. Thus, developing processing methods to integrate nanocomposites in the fabrics is essential for exploiting their properties for medical textiles.

In this study, polypropylene fabrics, alginate and copper oxides, were selected to develop novel antimicrobial nanocomposites based on various surface treatments, i.e. corona discharge and alginate impregnation, which led to improved fabrics hydrophilicity with functional groups introduced as binding sites for Cu(II), a precursor that formed Cu nanoparticles when reacted with reducing agents, i.e. NaBH₄ and ascorbic acid. The composition of the fabrics after being treated with corona discharge and impregnation observed by XPS indicates the materials formed mainly consisted of C and O, attributed to the presence of a thin, hydrophilic layer and alginate, respectively, consistent with depth profiling measurements. Following Cu reduction, XPS mapping of the fabrics finds that, reacting with ascorbic acid resulted in formation of nanocomposites containing a mixture of Cu and Cu (II) oxides across the surface, which could be visualised by using SEM in the same locations. Excellent anti-microbial activity against Gram-negative bacteria *E. coli*, Grampositive bacteria *S. aureus* and yeast *C. albicans* was observed for the treated fabrics[2]. This result not only demonstrates a cleaner, and healthier approach for developing novel nanocomposites, but more importantly highlights the role of surface

techniques in uncovering challenges in designing and engineering functional textiles.

References:

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9:00am AS+2D+CA+EL+EM+MS+NS+SE+SS+TF-WeM-4 **Multi-Modal Analysis in Photoelectron Spectroscopy: From High-Resolution Imaging to Operando Experiments**, Olivier Renault, CEA-Leti, France; A. Benayad, CEA, France; N. Gauthier, CEA-Leti, France; R. Charvier, ST Microelectronics, France; E. Martinez, CEA-Leti, France

Over the past years, the field of surface and interface analysis has been greatly expanded by new developments made possible by lab-scale instruments enabling higher excitation energies. These new developments are directly serving technological advances especially in the area of technologies in renewable energies and nanoelectronics, which are addressing more and more complex system requiring to go beyond traditional ways of characterizing surfaces and interfaces. Different dimensions are to be explored in multi-modal surface analysis : the depth dimension, the lateral dimension, and the dynamic dimension.

After a short review of some of the achievements towards enhancing the depth dimension by lab-scale hard X-ray photoelectron spectroscopy (HAXPES) and the lateral dimension using X-ray PEEM, we will present different application cases of *operando* HAXPES. Here, the material is analyzed as being part of a device operated *in situ* during the experiment, in conditions that are as close as possible to the final applications and where the interfaces can be studied in dynamic conditions. We will first review some results of *operando* HAXPES on resistive memories obtained with synchrotron radiation [1, 2] before presenting various lab-scale experiments [3, 4] and the current limitations to such approaches.

[1]B. Meunier, E. Martinez, O. Renault et al. *J. Appl. Phys.* **126**, 225302 (2019).

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9:20am AS+2D+CA+EL+EM+MS+NS+SE+SS+TF-WeM-5 **Multi-Modal Analyses of Ultrasonic-Spray-Deposited Ultrathin Organic Bathocuproine Films**, J. Chen, Juliet Risner-Jamtgaard, T. Colburn, A. Vailionis, A. Barnum, M. Golding, Stanford University; K. Artyushkova, Physical Electronics; R. Dauskardt, Stanford University

Bathocuproine (BCP) is a small organic molecule that is typically used as an ultrathin hole blocking interlayer (< 10 nm thickness) in organic solar cells and perovskite solar cells. The film is typically deposited via low-throughput vacuum thermal evaporation with an *in-situ* Quartz Crystal Monitor to measure film thickness. Open-air ultrasonic spray deposition for low-cost and large-scale deposition is an attractive alternative method for solution processing of BCP films, but the process lacks a comparable *in-situ* metrology. Given that the BCP film is transparent to visible light and ultrathin, it is important to utilize a multi-modal approach to evaluate optoelectronic and physical properties of the sprayed film.

A suite of characterization techniques that span a range of equipment complexity, measurement time, and measurement sensitivity are used to analyze the BCP films. We begin by demonstrating the limitations of the singular ellipsometry model¹ for BCP found in literature and motivate a need to rely on other techniques. Multi-modal analyses including X-Ray Reflectivity, Angle-Resolved X-ray Photon Spectroscopy (AR-XPS), Auger Spectroscopy, Scanning Electron Microscopy, and Transmission Electron Microscopy with EELS are then performed on the sprayed BCP film. The advantages and disadvantages of each characterization technique are compared and discussed. We conclude that AR-XPS provides the most distinctive determination of individual layer thicknesses for a sample architecture consisting of silicon substrate/native SiO₂/BCP across the applicable range of AR-XPS from ~ 1-10 nm.

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^[1]Liu, Z.T., *et al.* The characterization of the optical functions of BCP and CBP thin films by spectroscopic ellipsometry. *Synthetic Materials*. 150(2):159-163. (2005)

9:40am **AS+2D+CA+EL+EM+MS+NS+SE+SS+TF-WeM-6 Combinatorial Synthesis and High-Throughput Characterization of Pt-Au Thin Films Fabricated by Confocal Magnetron Sputter Deposition, David Adams, R. Kothari, M. Kalaswad, C. Sobczak, J. Custer, S. Addamane, M. Jain, E. Fowler, F. DelRio, M. Rodriguez, R. Dingreville, B. Boyce, Sandia National Laboratories**

A few binary metal alloys are predicted to form thermally stable, compositionally segregated structures owing to the thermodynamic preference for minority species to collect and remain at grain boundaries established within the solid. (J.R. Trelewicz *et al.*, PRB, 2009) When produced as a nanocrystalline thin film, these stable structures afford the potential to maintain excellent mechanical properties (e.g., high hardness) even after annealing to elevated temperature. Indeed, several systems, including Pt₉Au₁ thin films, are reported to develop thermally-stabilized, hard, nanocrystalline structures attributed to solute segregation at grain boundaries. (P. Lu *et al.*, *Materialia*, 2019)

Future studies that seek optimal stoichiometry and/or preferred synthesis processes require access to a wide range of composition as well as an ability to vary key deposition parameters. Toward this end, our team reports on the challenges and the benefits of combinatorial synthesis for expediting the discovery of improved binary metal thin films. Our study utilized confocal sputter deposition wherein Pt and Au targets were individually sputtered via pulsed DC magnetron methods. Substrates (150 mm diameter wafers) were fixed in order to gain access to a wide compositional range for each deposition. The sputter power and cathode tilt orientation were then varied in subsequent depositions to access the nearly full binary metal compositional range. The binary collision Monte Carlo program SiMTra (D. Depla *et al.*, *Thin Solid Films* 2012), which simulates the transport of sputtered atoms within the process gas, helped guide the selection of these process parameters in order to achieve compositional goals in relatively few depositions. Notably, the binary compositions predicted by SiMTra closely matched (within a few molar %) the measured compositions determined by Wavelength Dispersive Spectroscopy completed in 112 different areas across each wafer. The various combinatorial Pt-Au films were further characterized by high-throughput Atomic Force Microscopy, automated X-ray Diffraction, fast X-ray Reflectivity, mapping four-point probe sheet resistance, and automated nanoindentation. These studies reveal how hardness, modulus, film density, crystal texture, and resistivity of combinatorial films varied with composition as well as the atomistics of film deposition. Attempts to correlate key film characteristics with the kinetic energies and incident angles of arriving metal species (estimated by SiMTra) are discussed with a goal of improving fabrication processes.

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11:00am **AS+2D+CA+EL+EM+MS+NS+SE+SS+TF-WeM-10 Optical and X-Ray Characterization and Metrology of Si/Si(1-x)Ge(x) Nanoscale Superlattice Film Stacks and Structures, Alain Diebold, SUNY Polytechnic Institute INVITED**

As traditional scaling of transistors comes to end, transistor channels and capacitors are being stacked to form new 3D transistor and memory devices. Many of these devices are fabricated using films stacks consisting of multiple Si/Si(1-x)Ge(x) layers known as superlattices which must be fabricated with near atomic precision. In this talk, we discuss how Optical and X-Ray methods are used to measure the feature shape and dimensions of these structures. The use of X-Ray methods such as ω -2 θ scans and reciprocal space maps provide layer thickness and stress characterization. We will use simulations to show how a buried layer with a different thickness or Ge concentration alters the data. Recent electron microscopy studies have quantified the stress at the interfaces of these superlattices. We will also discuss how Mueller Matrix spectroscopic ellipsometry (MMSE) based scatterometry is used to measure feature shape and dimension for the nanowire/nanosheet structures used to fabricate nanosheet transistors and eventually 3D DRAM. The starting point for optical scatterometry is determining the optical properties of stressed pseudomorphic Si(1-x)Ge(x). MMSE can be extended into the infra-red and into the EUV. In addition, small angle X-Ray scattering has been adapted into a method known as CDSAXS which can be used to characterize these structures. This talk will be an overview of these methods.

11:40am **AS+2D+CA+EL+EM+MS+NS+SE+SS+TF-WeM-12 Non-Destructive Depth Differentiated Analysis of Surfaces Using Ion Scattering Spectroscopy (ISS), XPS and HAXPES, Paul Mack, Thermo Fisher Scientific, UK**

Recently there has been renewed interest in probing deeper into surfaces using HAXPES in addition to the more surface sensitive (soft X-ray) XPS. On modern XPS systems, with high sensitivity, the total sampling depth may be somewhere between 10nm and 15nm but HAXPES enables the analyst to look deeper, without having to destructively sputter the surface with ions. For a complementary, more comprehensive analysis, XPS and HAXPES can be combined with Ion Scattering Spectroscopy (ISS). ISS is far more surface sensitive than XPS, typically being thought of as a technique to analyse the top monolayer of a sample for elemental information.

In this work, the combination of XPS, HAXPES and ISS on a single tool has been used to give a non-destructive depth differentiated analysis of a range of samples, including a perovskite and an industrially relevant material containing multiple transition metals. The combination of all three techniques provides insight into the depth distributions of elements and chemical states, from the top monolayer to beyond 20nm into the surface.

12:00pm **AS+2D+CA+EL+EM+MS+NS+SE+SS+TF-WeM-13 Towards Measurement of Molecular Shapes Using OrbiSIMS, Gustavo F. Trindade, J. Vorng, A. Eyres, I. Gilmore, National Physical Laboratory, UK**

An OrbiSIMS [1] instrument features a dual analyser configuration with a time-of-flight (ToF) mass spectrometer (MS) and an OrbitrapTM MS, which confer advantages of speed and high-performance mass spectrometry, respectively. The ability to combine the MS performance usually found in a state-of-the-art proteomics and metabolomics MS with 3D imaging at the microscale and from nanolayers of <10 nm of material has proved popular in a broad field of application from organic electronics to drug discovery. For secondary ions to be efficiently transferred to the Orbitrap analyser, the sample is biased by a target voltage V_T necessary to match the acceptance window of the Orbitrap. Furthermore, the ions kinetic energy from the SIMS collision process must be reduced. Therefore, in the OrbiSIMS, a transfer system with helium gas at a pressure P_{He} slows the ions and reduces their kinetic energy distribution through inelastic collisions with gas atoms. Usually, an Orbitrap is used with an ambient pressure ion source and so here an extra gas flow of nitrogen is introduced that leads to an increase of pressure P_{N_2} to compensate.

We conducted a systematic assessment of V_T and P_{He} and P_{N_2} on the transmitted secondary ion intensities [2] and revealed a complex behaviour, indicating the possibility for additional separation of ions based on their shape, stability, and kinetics of formation. We showed that the V_T for maximum transmission of secondary ions will not be the same for all molecules of the same material and that sometimes multiple maxima exist. Here, we present recent progress towards the understanding of these phenomena and how we are leveraging it to measure molecular shape by using reference trisaccharides raffinose, maltotriose and melizitose [3].

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[3] G.F. Trindade *et al.*, In preparation.

Electronic Materials and Photonics Division Room B116 - Session EM-WeM

Advancements in Microelectronics and Nanotechnology by Early and Mid Career Professionals

Moderators: Erica Douglas, Sandia National Laboratories, Stephen McDonnell, University of Virginia

8:00am **EM-WeM-1 Assessment and Benchmarking of Nonvolatile Memory Devices for Analog In Memory Computing, Matthew Marinella, Arizona State University; C. Bennett, P. Xiao, W. Wahby, S. Agarwal, Sandia National Laboratories INVITED**

Deep neural networks (DNNs) have garnered significant recent attention due to the revolutionary new capabilities they are enabling. These

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advancements have been made possible by the exponential increase in performance and energy efficiency of digital computing hardware over the past several decades. However, digital DNN accelerators are hitting ultimate limits of around 1-10 teraoperations per second per watt (TOPS/W) – and for progress to continue, new computing paradigms are needed. Analog in-memory computing (AIMC) is an architecture which promises to enable > 100 TOPS/W by efficiently processing the analog vector matrix multiply (VMM) operation at the heart of DNN algorithms – enabling capabilities well beyond what is possible with digital systems. The VMM operation is performed using an array of nonvolatile memory devices, which are programmed to represent a matrix of network weights through their conductance states. An input to this array is scaled to represent a vector, and each multiply is carried out using ohms law, followed by the accumulation of currents down each column. Many devices are under consideration for use with AIMC, including the flash memory cell (charge trapping and floating gate), and emerging resistive memory (ReRAM), conducting bridge memory (CBRAM), and electrochemical memory (ECRAM). The use of these devices for AIMC represents a significant departure from using the same devices for digital memory in that the neural network classification accuracy depends directly on the nuanced device-level behavior of nonvolatile memories. Device properties such as programming variability, read noise, drift, write linearity, and symmetry must be characterized in detail to form a dataset that can be used to model the accuracy of a DNN algorithm, when executed on an AIMC processor using that particular nonvolatile memory. For example, we have electrically characterized SONOS and ReRAM devices and simulated the classification accuracy for an AIMC accelerator running ImageNet on ResNet50 – which is a common machine learning benchmark. This talk will overview the process of benchmarking nonvolatile memory devices for AIMC, including electrical characterization, dataset generation, and process of modeling DNN accuracy based on this data. SNL is managed and operated by NTESS under DOE NNSA contract DE-NA0003525.

8:40am **EM-WeM-3 AVS Peter Mark Memorial Award Talk: Heterostructures for Low-Power Logic and Memory Devices, Deep Jariwala**¹, University of Pennsylvania **INVITED**

The isolation of a growing number of two-dimensional (2D) materials has inspired worldwide efforts to integrate distinct 2D materials into van der Waals (vdW) heterostructures. While a tremendous amount of research activity has occurred in assembling disparate 2D materials into “all-2D” van der Waals heterostructures and making outstanding progress on fundamental studies, practical applications of 2D materials will require a broader integration strategy. I will present our ongoing and recent work on integration of 2D materials with 3D electronic materials to realize logic switches and memory devices with novel functionality that can potentially augment the performance and functionality of Silicon technology. First, I will present our recent work on gate-tunable diode¹ and tunnel junction devices² based on integration of 2D chalcogenides with Si and GaN. After that I will present phase control growth and integration strategies for 2D In chalcogenides at back end of line (BEOL) compatible temperatures.³

Following this I will present our recent work on non-volatile ferroelectric memory devices based on AlScN.⁴ First, I will present on Ferroelectric Field Effect Transistors (FE-FETs) made using a heterostructure of MoS₂/AlScN^{5,6} and also introduce our work on Ferroelectric Diode (FeD) devices also based on thin AlScN.⁷ In addition, I will also present how FeDs provide a unique advantage in compute-in-memory (CIM) architectures for efficient storage, search as well as hardware implementation of neural networks.⁸

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9:20am **EM-WeM-5 BeyondFingerprinting – Materials Discovery via High-Throughput, Low Cost, AI-Guided Materials Science, B. Boyce, R. Dingreville, Elliott Fowler, N. Trask, D. Adams, J. Coleman, K. Johnson, Sandia National Laboratories**

In 1957 Richard Bellman first introduced the ‘Curse of Dimensionality’ – describing how the number of samples needed to estimate an arbitrary function with a given level of accuracy grows exponentially with respect to the number of input variables [1]. Almost 70 years later, the field of Materials Science is still grappling with the Curse. Despite significant advances in capability and speed in materials synthesis and characterization since Bellman’s observation, most materials discovery challenges are far too high dimensional in terms of both inputs and material properties to brute force through with high throughput experimentation alone [2]. Thus, artificial intelligence (AI) and machine learning (ML) are increasingly being utilized because they allow for the rapid development of process-structure-property-performance relationships across a vast material domain. These AI/ML frameworks are designed to take high dimensional search spaces and significantly reduce them into strongly correlated latent spaces. The core question motivating Sandia’s *BeyondFingerprinting* Grand Challenge is: *How do you merge scientific data with a range of dimensionalities and uncertainties from multiple disparate sources (both experiments and high-fidelity simulations) to extract the most meaningful information through advanced machine learning algorithms?* In this talk, I will discuss how *BeyondFingerprinting* is addressing this question with a two-fold approach, including development of high throughput, low-cost data streams and Himulaya (Hybrid-Informed Multi-Layered Algorithms), across three distinct material exemplars: Laser Powder Bed Fusion, Electrodeposition and Physical Vapor Deposition. Furthermore, I will show how this framework is enabling the acceleration of material discoveries across each of these three domains through discussion of combinatorial synthesis (100s of samples per day) and high-throughput characterization (1000s of measurements per week) strategies, as well as data management and AI/ML approaches. Perspective will be provided on how advances in *BeyondFingerprinting* might impact the development of Electronic Materials and Devices.

[1]L. Chen, "Curse of Dimensionality," in *Encyclopedia of Database Systems*, L. Liu and M. T. Özsu Eds. Boston, MA: Springer US, 2009, pp. 545-546.

[2]E. J. Amis, X.-D. Xiang, and J.-C. Zhao, "Combinatorial materials science: What's new since Edison?," *MRS bulletin*, vol. 27, no. 4, pp. 295-300, 2002.

9:40am **EM-WeM-6 Tunability of the Thermal and Photophysical Properties of Blue-Emitting Fluoranthene Chromophores, Christopher Brewer, J. Wheeler, A. Pynch, F. Castellano, North Carolina State University**
Designing organic blue-emitting chromophores with properties suitable for applications in devices, such as OLEDs, is a challenging task. Organic blue-emitting chromophores often have broad emission profiles and do not sublime cleanly for device fabrication. Consequently, organometallic blue emitters are more readily used in device applications due to their desirable thermal and photophysical properties. Despite these drawbacks, fluoranthene is a potential organic scaffold for designing blue-emitting organic chromophores. Fluoranthene’s modular synthetic approach allows for nearly limitless functional group modification. Additionally, modifying its functional groups can tune fluoranthene’s thermal and photophysical properties. Most notably, the volatility of the fluoranthene can be increased by installing trifluoromethyl substituents, while the volatility decreases when substituents such as methoxy are utilized. To date, our deepest blue-emitting fluoranthene chromophore (CIE 1931: 0.156, 0.111) incorporates trifluoromethyl and methoxy substituents while retaining desirable thermal properties. Ultimately, the vast array of synthetic modifications available with the fluoranthene scaffold makes this organic chromophore suitable for device fabrication, as both the emission and volatility can be controlled. This talk will discuss the photoluminescence of fluoranthene derivatives in both the solid and solution state, as well as the substituent influence on the volatility of the molecule.

11:00am **EM-WeM-10 Hf-Doping of Polycrystalline Gallium Oxide Thin-films, Seth King, University of Wisconsin - La Crosse**

Hafnium (Hf) doping of Ga₂O₃ single crystals has shown that Hf occupies an octahedrally coordinated Ga site and behaves as an n-type dopant [1-3]. However, these reports have only studied a single concentration of Hf incorporated into melt grown Ga₂O₃ single crystals. To gain insight into how Hf concentration impacts the optical, structural, and morphological properties of the material, polycrystalline Hf-doped Ga₂O₃ were deposited by RF-sputtering onto silicon and fused silica substrates at room

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temperature. Deposited films, with varying concentrations of Hf, were subsequently characterized by spectroscopic ellipsometry, UV-Vis spectrophotometry, x-ray diffraction, x-ray photoelectron spectroscopy, and atomic force microscopy both in the as-deposited state and upon subsequent, ex-situ annealing.

Results show that all films, regardless of Hf concentration, are initially amorphous, but crystallize as β -Ga₂O₃ upon annealing. Spectroscopic ellipsometry measurements show that the index of refraction of the film is altered by Hf incorporation, while UV-Vis measurements show that the optical bandgap is not significantly altered. These results suggest that Hf-doped Ga₂O₃ may find use in optoelectronic devices and applications.

[1] <https://iopscience.iop.org/article/10.1088/1361-6641/ab75a6>

[2] <https://aip.scitation.org/doi/10.1063/5.0062739>

[3] <https://doi.org/10.1063/5.0062739>

11:20am **EM-WeM-11 Composition of Chemically Treated (111) Surfaces of Cd_{0.9}Zn_{0.1}Te by X-Ray Photoelectron Spectroscopy**, *H. Yuan, T. Nguyen, Thomas Tiedje*, University of Victoria, Canada; *B. Aitchison, Y. Song, M. Jackson*, Redlen Technologies, Canada; *J. Chen, H. Wang*, University of Saskatchewan, Canada

Cd_{0.9}Zn_{0.1}Te (CZT) x-ray detectors have enabled high performance medical x-ray imaging systems. The surface properties of CZT are important in x-ray detector applications as they influence performance through their effects on electron-hole injection and collection. In this work, the composition of 111A surfaces of CZT single crystals were investigated following chemical etching with Br₂/methanol and HCl, vacuum annealing, ozone oxidation and H₂S exposure. Both synchrotron and lab-based X-ray photoelectron spectroscopy (XPS) were used to investigate changes in the surface composition and interfacial band alignment of treated CZT surfaces.

Chemical etching with Br₂/methanol was used to remove polishing damage, and leaves 4-6 monolayers of excess Te on the surface depending on the etch time and composition of the etch. HCl etching removes surface oxides formed by air exposure or by exposure to UV-generated ozone, leaving elemental Te (Te⁰) on the surface. Residual Te⁰ was removed by vacuum annealing at 250°C for one hour. XPS and Raman spectroscopy measurements on the vacuum annealed samples confirm the formation of a stoichiometric CZT surface. We were able to grow a mixed CZT-oxide about 8 nm thick by UV ozone exposure in air at room temperature for 1 hr. Depth profiles of the surface composition were obtained from the energy dependence of the photoelectron escape depth, accessible with the tunable x-ray energy available from the synchrotron source. We found a non-uniform vertical composition profile with CdO on the surface and Te⁰ and TeO₂ underneath, suggesting that Cd out diffuses during oxidation.

Vacuum annealed and ozone oxidized surfaces were exposed to 500 ppm H₂S in N₂ in a tube furnace at 250 °C and 280 °C for 0.5-2 hr. SEM/EDX imaging and ellipsometry measurements indicate that a 50-60 nm CdS layer is formed after 2 hr exposure to H₂S at 280 °C. The ozone oxidized starting surface was found to be more reactive with H₂S than the vacuum annealed surface. Sulfided surfaces were depleted in Te and O leaving a surface layer rich in CdS similar to the results of Nelson and Levi [1] with H₂S plasma treatment. We are exploring the effect of the various surface treatments on x-ray detector performance.

[1] A. J. Nelson, D. Levi, Novel method for growing CdS on CdTe surfaces for passivation of surface states and heterojunction formation, *JVST A*, 15, 1119 (1997).

11:40am **EM-WeM-12 High Throughput Design of 2D Electronic Materials and Heterostructures**, *Nicholas Glavin*, Air Force Research Laboratory, Materials and Manufacturing Directorate, USA **INVITED**

2D materials represent an exciting opportunity to create tunable heterostructures for next generation electronic applications. In this talk, strategies and processes to enable high throughput design and customization of 2D materials which enable novel, multifunctional properties is presented. These techniques include rapid laser-manufacturing approaches, where high throughput structure/property evaluation can allow for rapid device design. This same process can be implemented in a roll-to-roll configuration to allow for manufacturing of ultralow cost 2D devices at scale for detection of a host of different sensing environments including detection of pathogens. Additionally, a two-step metal conversion process will be discussed that allows for direct synthesis of 2D transition metal dichalcogenide superlattices which can result in 3D heterostructures of interest to future applications.

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Applied Surface Science Division

Room B117-119 - Session AS+CA+EL+EM+SE+SS+TF-WeA

Quantitative Surface Analysis I

Moderators: David Cant, National Physical Laboratory, UK, Peter Cumpson, University of New South Wales, Christopher Moffitt, Kratos Analytical Inc, Lev Gelb, University of Texas at Dallas

2:20pm AS+CA+EL+EM+SE+SS+TF-WeA-1 Status of Efforts to Upgrade the Quality of Surface Analysis Data in the Literature, Donald Baer, Pacific Northwest National Laboratory

Multiple efforts are being undertaken to address a growing presence of faulty surface analysis data and/or analyses appearing in the literature. Issues include bad data, incorrect analysis, and highly incomplete reporting of instrument and analysis parameters. This talk describes the status of four efforts to address some of the issues. Recognition of this problem within the surface analysis community has increased with an understanding that both inexperienced users and increased use of surface analysis methods outside the surface analysis community contribute to the problem. The current efforts build upon decades of development and efforts by standards committees, excellent books and journal publications, websites, short courses, and other efforts. A collection of guides, protocols and tutorials addressing reproducibility issues with a significant focus on XPS was published in JVSTA in 2020/21. A second collection, *Reproducibility Challenges and Solutions II*, with a more general focus on Surface and Interface Analysis was initiated in 2022 and is being finalized. The second collection addresses several techniques, including SIMS, SPM, and UPS, and includes topics such as theoretical modeling and machine learning in data analysis. A second effort focuses on a part of the community less interested in general understanding but needs to answer specific surface analysis questions. A new type of paper called Notes and Insights is being published in the journal Surface and Interface Analysis with the objective to provide incremental bits of useful information of importance to non-expert analysts. Two additional activities are underway to assist with reporting issues. Examination of papers in multiple journals found that instrument and analysis related information needed to assess or reproduce data is often incomplete or absent. To assist authors in reporting instrument parameters, papers describing in some detail related families of commercial instruments are being prepared for Surface Science Spectra. These papers describe the instrument, major components, geometry and provide example data related to common data collection modes. Authors will be able to reference these papers and identify specific modes of instrument operation used in their research. Another parameter reporting activity concerns sample handling before analysis. ISO Technical Committee 201 is developing a series of documents (ISO 20579 parts 1 to 4) on what needs to be reported regarding sample handling, storage, processing, and mounting for analysis. These standards describe what needs to be reported and contain informative annexes that provide information regarding the needs and challenges to proper sample handling to produce reliable useful surface analysis data.

2:40pm AS+CA+EL+EM+SE+SS+TF-WeA-2 The behavior of the Shirley background of the Ti 2p spectra across the Ti 1s edge, Dulce Maria Guzman Bucio, CINVESTAV-Unidad Queretaro, Mexico; D. Cabrera German, Universidad de Sonora, Mexico; O. Cortazar Martinez, J. Raboño Borbolla, CINVESTAV-Unidad Queretaro, Mexico; M. Vazquez Lepe, Universidad de Guadalajara, Mexico; C. Weiland, J. Woicik, National Institute of Standards and Technology; A. Herrera Gomez, CINVESTAV-Unidad Queretaro, Mexico
A wide variety of photoemission spectra display a step-shaped background, called the Shirley-type background, which should be accounted for in the total background signal for reliably assessing chemical composition. However, it cannot be modeled with any method based on extrinsic processes like the inelastic dispersion of the photoelectrons (e.g., Tougaard-type backgrounds). Although its physical origin is still unknown, experimental data suggest that the Shirley-type background is due to phenomena occurring inside the atom [1,2]. To gain insights into those phenomena, we studied the behavior of the Shirley-type background for the Ti 2p photoemission spectra.

In this work, Ti 2p photoemission spectra were acquired with Synchrotron light (at Beamline 7-2 at the Brookhaven National Laboratory) from a clean metallic titanium film (sputtered on a Si (100) substrate) capped with an

ultra-thin aluminum layer. The spectra were collected with 44 excitation energies around the Ti 1s edge. By simultaneously fitting Ti 2p photoemission spectra obtained with excitation energies higher than the Ti 1s edge, we robustly determined the peak structure of the Ti 2p spectra. Outstandingly, the parameter of the Shirley-type background associated with the Ti 2p peak structure is modulated as the photon energy crosses the Ti 1s edge. The relation of this phenomenon with the physical origin of the Shirley background will be discussed. The KVL_{2,3} Auger peaks—which overlap with the Ti 2p peaks—do not have a step-shaped background for most of the excitation energies.

Acknowledgments:

Use of the Brookhaven National Laboratory is supported by the U.S. Department of Energy's (DOE) Office of Science.

This work was partially financed by CONACyT Project Fronteras 58518, Mexico.

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- [2] A. Herrera-Gomez, Interchannel Coupling with Valence Band Losses as the physical origin of the Shirley background in photoemission spectra (Old title: The unresolved physical origin of the Shirley background in photoemission spectra), Queretaro, 2015. <http://www.qro.cinvestav.mx/%0A~aherrera/reportesInternos/unknownOri ginShirley.pdf>.

3:00pm AS+CA+EL+EM+SE+SS+TF-WeA-3 Chemical Analysis of Multilayer System by Photoemission: The Binding Energy Reference Challenge, Thierry Conard, A. Vanleenhove, IMEC Belgium; D. Desta, H. Boyen, University of Hasselt, Belgium

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

Increasing the number of analyzed (insulating) layers enhances the risk of significant vertical differential charging and makes the repeatability of binding energy determination more challenging. While charging has to be taken into account for XPS, the analysis of most XPS spectra is quite straightforward as long as the surface charge is stable and the lateral distribution of surface charge is uniform within the area of analysis. For HAXPES however vertical charge distribution comes into the game for a large group of structures whose development can benefit from HAXPES analysis. Vertical charge build-up can be complex, especially if examined structures exist of multiple layers and hence multiple interfaces, containing a large variety of materials. But even in 'simple' non-conducting one-layer structures a vertical charge gradient builds up when exposed to X-rays and small changes in the parameters of standard surface charge neutralization techniques - as the use of e-beam flood guns - can influence the nature of the charge gradient.

In this work, we will examine the influence of measurement conditions in single and multiple layers systems relevant to the microelectronic industry on the determination of precise binding energies.

HAXPES spectra of technologically relevant samples will be discussed to demonstrate the challenge of determining exact binding energy values. The set of examined samples comprises oxide layers Si samples and metal/high-k/Si stacks including high-k materials as HfO₂ and Al₂O₃. The surface potential will be precisely set and monitored in situ by depositing a metallic layer (such as Ag) on top of the stack and applying an external potential instead of using an electron neutralization source. All experiments are performed in a PHI Quantex system and/or a Scienta Omicron HAXPES Lab, both equipped with two monochromatic X-ray sources: an Al K α (1486.6 eV) and a Cr K α (5414.8 eV - Quantex) or Ga K α (9252.1 eV - HAXPES lab) X-ray source.

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3:20pm **AS+CA+EL+EM+SE+SS+TF-WeA-4 Where Are We on the Road-Map to Artificially Intelligent Interpretation of X-ray Photoelectron Spectra?**, C. Moffitt, Kratos Analytical Inc; A. Roberts, J. Counsell, C. Blomfield, Kevin Good, K. Macak, Kratos Analytical Limited, UK

Robust peak identification is crucial for accurate sample analysis using X-ray photoemission spectroscopy (XPS). Automation of peak ID enhances this process by minimizing user error and bias. Current acquisition software offers improved computer-derived peak identification from unknown samples, instilling confidence in the correct identification of elements. Moreover, this forms the foundation for an automated sample analysis workflow known as Data-dependent Analysis (DDA). DDA involves identifying peaks in a survey spectrum and subsequently acquiring high-resolution spectra from major components. A recent User survey revealed that a significant majority of users rely on the large area survey acquisition mode as a starting point for analysis.

To provide a metric for confidence in the DDA process, existing spectral analysis data, which includes the element composition information, is used to generate reference spectra for testing purposes. These reference spectra serve as the basis dataset against which the performance of the automated analysis algorithm can be evaluated. By comparing the results of the algorithm with the reference spectra, statistical parameters can be calculated to assess the algorithm's precision, sensitivity, specificity, and accuracy in identifying elements of unknown spectra.

For experienced analysts, DDA serves as a time-saving acquisition method, while for inexperienced analysts, it provides assurance in accurate peak identification and appropriate high-resolution spectra acquisition. Here we highlight current status of automated XPS data acquisition in relationship to the 'expert system', championed in the early 2000's and full AI interpretation of XPS spectra of the future.

4:20pm **AS+CA+EL+EM+SE+SS+TF-WeA-7 Thin Film Analysis by XPS: Quantitative Analyses Using Physics-Based and Machine-Learning Approaches**, Lev Gelb, N. Castanheira, A. Walker, University of Texas at Dallas

We present progress towards quantitative analysis of XPS data using both model-based "fitting" approaches and machine learning methods. Two separate applications are considered.

The first concerns the simultaneous extraction of both compositional profiles and sputtering parameters from XPS sputter depth-profiles of multilayer films. Depth-profile data are routinely processed to provide "fractional composition vs ion dose" profiles, but such analyses typically assume the sample is homogeneous in the probed region, which is not true near interfaces, and cannot precisely convert between units of ion dose and depth without extensive calibration data. Our approach is to first construct analytical models for both the sample structure and for the sputtering process, and then to determine the model parameters (layer thicknesses, interfacial widths, material removal rates, etc.) that are most likely given the observed apparent fractional composition profiles. This is done numerically, by iteratively comparing simulated and observed apparent composition profiles. The only additional required inputs are the inelastic mean free paths for each tracked peak in each material present. The efficacy of this approach is demonstrated using both synthetic and experimental data sets, and various model improvements (sputter-induced mixing, *in situ* chemical reactions) are discussed.

The second application concerns the application of machine-learning tools to remove the inelastic scattering background from XPS spectra in order that accurate peak areas can be obtained. Our approach here is to generate a training data set which consists of a thousands of simulated XPS spectra with and without inelastic scattering included. This is accomplished using the SESSA software package[1]. This data set is then used to train a neural network algorithm to output a "no-background" spectrum from an input "with-background" spectrum; this output spectrum can then be used to compute peak areas for compositional analysis. The training set generation methodology and network structure are discussed, and application of the tool to both simulated and experimental spectra is demonstrated.

[1] Werner, W., Smekal, W., Powell, C. and Gorham, J. (2021), *Simulation of Electron Spectra for Surface Analysis (SESSA) Version 2.2 User's Guide*, Natl Std. Ref. Data Series (NIST NSRDS), <https://doi.org/10.6028/NIST.NSRDS.100-2021>.

4:40pm **AS+CA+EL+EM+SE+SS+TF-WeA-8 Room Temperature Ionic Liquids as Reference Materials for Photoelectron Spectrometers**, Benjamin Reed, National Physical Laboratory, U.K.; J. Radnik, BAM Berlin, Germany, UK; A. Shard, National Physical Laboratory, U.K.

Room-temperature ionic liquids (RTILs) are materials consisting of organic salts that are liquid below temperatures of 100°C and are used in several fields including electrochemistry,¹ pharmaceuticals, and medicine.² RTILs have several notable properties that make them ideal for X-ray photoelectron spectroscopy (XPS) analysis. They have an extremely low vapor pressure and high surface tension, and so can be analysed using conventional XPS under ultrahigh vacuum without the need for near-ambient pressure instrumentation. Also, when deposited in a recessed sample holder, the meniscus of an RTIL will be perfectly flat meaning that there are no contributions from sample topographic effects. Finally, and most importantly, they are highly homogeneous and have well-defined stoichiometries.³

These properties make RTILs potential reference materials for validating the intensity calibration of a photoelectron spectrometer. RTILs with non-coordinating bistriflimide (NTf₂) anions (e.g. PMIM⁺NTf₂⁻) or dimethyl phosphate (DMP) anions (e.g. MMIM⁺DMP⁻) are such candidates, with core levels up to ~800 eV binding energy, making them apt for verifying the quantification of light elements, especially for organic materials.^{4,5}

To accurately determine peak areas, however, requires the principal and secondary photoelectron signals to be deconvolved. Previous attempts by multiple laboratories using different quantification methods give a mean atomic composition within 1 at.% of the known stoichiometry, but some individual elements (such as fluorine) exhibit differences greater than 1 at.% because the elastic and inelastic secondaries are not suitably deconvolved. Attention must be paid to the energy loss function that defines the inelastic background over the full energy range of an XPS spectrum so that a suitable Tougaard background subtraction can be applied.⁶ Here we present a study on several RTILs and discuss how they may be used to validate an XPS intensity calibration and provide confidence in measurements to XPS instrument operators.

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²K. S. Egorova, E. G. Gordeev, and V. P. Ananikov, *Chem. Rev.* **117**, 7132 (2017).

³E. F. Smith, I. J. Villar Garcia, D. Briggs et al., *Chem. Commun.* **45**, 5633 (2005).

⁴B.P. Reed, J. Radnik, and A.G. Shard, *Surf. Sci. Spectra* **29**, 014001 (2022).

⁵X. Knigge and J. Radnik, *Surf. Sci. Spectra* **30**, 014006 (2023).

⁶M. P. Seah, I. S. Gilmore, and S. J. Spencer, *Surf. Sci.* **461**, 1 (2000).

5:00pm **AS+CA+EL+EM+SE+SS+TF-WeA-9 Fractional Coverage Analysis of Monolayers with XPS and Non-Destructive Depth-Profiling with Combined Soft and Hard X-Rays**, Norbert Biderman, K. Artyushkova, D. Watson, Physical Electronics USA

X-ray photoelectron spectroscopy (XPS) is a well-established technique for non-destructive analysis of the chemical composition of thin layers and interfaces. Angle-resolved XPS (AR-XPS) has been used to determine composition of depth profiles and layer thicknesses, traditionally with Al K α (1486.6 eV) X-ray beams for depths up to 5-10 nm below the surface. In recent years, new AR-XPS capabilities have been added to Physical Electronics XPS scanning microprobe instruments including Cr K α (5414.8 eV) hard X-ray photoelectron spectroscopy (HAXPES) that can probe buried interfaces up to 15-30 nm below the surface. Coinciding with the HAXPES development, the StrataPHI analysis software was developed to reconstruct quantitative, non-destructive XPS/HAXPES depth profiles from angle-dependent and single-angle photoelectron spectra.

In this talk, we will show that the StrataPHI software has been further developed to combine Al K α and Cr K α XPS and HAXPES data within a single depth profile to enhance extracted analytical information from various depths below the surface. We will explore the method of the combined technique as well as its application to multilayered thin film samples. The updated StrataPHI software also includes a fractional coverage analysis mode, relevant in situations where ultra-thin films exist as discrete islands – commonly observed in early thin-film deposition stages on the substrate rather than as a continuous, uniform film. A model system of discrete molybdenum sulfide (MoS₂) monolayer triangles deposited on SiO₂/Si substrate will be discussed.

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Such added StrataPHI capabilities allow for scientists and engineers in metrology and research & development to analyze multi-layered thin films and ultra-thin films rapidly and non-destructively without potentially damaging ion beam sputtering that might otherwise be required to depth-profile or sputter-clean adventitious contamination off the surface.

5:20pm **AS+CA+EL+EM+SE+SS+TF-WeA-10 Reassessing the Reduction of Ceria in X-Ray Photoelectron Spectroscopy, David Morgan**, Cardiff University, UK

Given its excellent redox abilities, the use of cerium dioxide (CeO_2 , ceria) and related materials in catalysis is widespread [1]. This $\text{Ce}^{3+}/\text{Ce}^{4+}$ redox shuffle allows for great catalytic ability and a method of correlation of catalytic activity to the state of ceria [2–4]. Given that catalysis is a surface mediated process, XPS is critical in the analysis of pre- and post-mortem materials.

Over the years there has been debate on the degree of reduction of CeO_2 during XPS analysis. Therefore, in continuation of our work on understanding the reduction of materials in modern spectrometers [5], we have investigated different cerium oxide preparations and shown that not only is the rate of reduction dependent on instrument type and experimental configuration (and hence appropriate analysis protocols should be implemented), but is also related to the morphology of the cerium which may, at least in part, account for the discrepancies in the degree of reduction in the literature. It is postulated that reduction rates could be used to indicate likely ceria morphology where other analysis is unavailable.

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Acknowledgements

This work acknowledges the EPSRC National Facility for XPS ('HarwellXPS'), operated by Cardiff University and UCL, under contract No. PR16195, and C.M.A. Parlett and X. Zhou for provision of nanostructured ceria materials.

5:40pm **AS+CA+EL+EM+SE+SS+TF-WeA-11 Using High Sensitivity – Low Energy Ion Scattering Spectroscopy (LEIS) to Unravel the Complex Nature of High Entropy Alloys, Matthias Kogler, C. Pichler**, Centre for Electrochemistry and Surface Technology (CEST GmbH), Austria; M. Valtiner, Vienna University of Technology, Austria

Complex metallic materials such as Multi-Principal Alloys (MPEAs) and High Entropy Alloys (HEAs) have emerged as a promising class of materials given their unique inherent characteristics. Excellent mechanical, thermal, and corrosion properties allow for a broad spectrum of applications. However, due to the multi-element nature of these alloys, characterisation of the composition and microstructure proves to be a challenging task.

Especially with regard to corrosion-protective passivation films, the complex correlations with the corrosion behaviour are fully unclear to date, and require an in-depth atomic level characterisation and rationalisation. However, the precise layer by layer structure of such passive films is particularly demanding to assess, since traditional techniques such as XPS (X-ray photoelectron spectroscopy) or AES (Auger electron spectroscopy) have analysis penetration depths of several nanometres and cannot reach

atomic layer resolution. However, to fully understand and quantify the passivation layer structure, such an atomic layer resolution of the surface region is necessary, due to the complexity of HEAs.

In order to obtain an exact understanding of the atomistic mechanism at the monoatomic layer level, High-Sensitivity - Low Energy Ion Scattering Spectroscopy (HS-LEIS), was applied, which provides the required monolayer sensitive resolution to study the passivation layers of such complex multi-component alloys. The unique surface sensitivity combined with the implementation of in-situ treatment methods enabled the real-time study of oxide layer growth, as well as the analysis of temperature-dependent changes in the elemental surface composition. Due to the high resolution achieved by static and dynamic sputter depth profile modes, we could determine the exact composition of the HEA passivation layer with resolution on atomic monolayer scale.

The findings provide the potential to significantly advance the current understanding of the passivation behaviour of MPEAs and HEAs, and the development of novel metallic materials with superior properties. Valuable insights for understanding the material characteristics for those highly advanced materials could thereby be generated.

Electronic Materials and Photonics Division Room B116 - Session EM-WeA

Advanced Materials for Electronic and Photonic Applications

Moderators: Parag Banerjee, University of Central Florida, Jason Kawasaki, University of Wisconsin - Madison, Stephen McDonnell, University of Virginia

2:20pm **EM-WeA-1 Mind the Gap: Integrating Materials and Engineering Research to Enable Advanced Electronics, Paul Lane**, National Science Foundation

INVITED

Continued advances in computing, communications, and energy technologies present tremendous challenges and opportunities. Underpinning developments have often progressed independent of the intended embodiment, delaying incorporation into next-generation technologies. This presentation will present a broad overview of NSF efforts to address challenges involved with integrating materials research with technological advances, focusing on semiconductors. Research is supported at the level of individual investigators and small teams through topical materials and engineering research programs and at a larger scale through centers and facilities. I will emphasize cross-directorate programs that play a critical role in these efforts, such as Designing Materials to Revolutionize and Engineer Our Future (DMREF), Future of Semiconductors (FuSE), and Future Manufacturing.

3:00pm **EM-WeA-3 Atomic Layer Deposition Defect Engineering of Step Tunneling MIIM Diodes, Shane Witsell, J. Conley**, Oregon State University

Asymmetric electrode metal/insulator/metal (MIM) tunnel diodes can perform as ultra-fast rectifiers for applications in THz energy harvesting and IR detection, but require low turn on voltage (V_{ON}) and low zero bias resistance (ZBR) as well as current-voltage asymmetry (f_{ASYM}) and non-linearity (f_{NL}). Combining bilayer insulators as tunnel barriers (MIIM diodes) can improve performance over conventional MIM diodes via asymmetric resonant tunneling or "step" tunneling [1]. Utilizing insulating materials with *intrinsic* defects can further improve η_{ASYM} and f_{NL} as defect levels in the smaller band gap insulator can provide additional conduction pathways [2]. Finally, it has also been demonstrated that intentionally introduced *extrinsic* defect levels, precisely introduced into the insulator using atomic layer deposition (ALD) [3] can be used to engineer MIM diode performance. In this work, we investigate the use of ALD to intentionally introduce impurity defect levels into the large bandgap insulator of dual insulator MIIM diodes.

Three Al/HfO₂/Al₂O₃/Pt MIIM diodes were investigated: (i) Ti doped: in which a two ALD cycle Ti defect layer was positioned within the middle of the Al₂O₃, and (ii) Ni doped: in which a two ALD cycle Ni defect layer was also positioned within the middle of the Al₂O₃, and (iii) an undoped control. ALD of HfO₂, Al₂O₃, NiO, and Ti₂O₅ was performed using TEMA/Hf₂O/H₂O, Ni(tBu₂DAD)₂/O₃, and TTIP/H₂O. For all devices, ALD was performed onto a bottom Pt electrode. After ALD, Al was e-beam evaporated through a shadow mask with 250 μm diameter holes to form top electrodes.

The Ni doped diodes were found to have improved maximum f_{ASYM} over the undoped control, but increased V_{ON} , likely due to suppression of conduction

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by to negative charge trapped at Ni defect levels lying energetically near or below the equilibrium Fermi level ($E_{F,equl}$) [4]. The Ti doped diodes showed slightly reduced leakage current, likely due to positive trapped charge in Ti defect levels near or above the $E_{F,equl}$, and also increased maximum f_{asym} . However V_{ON} was not reduced. Compared to the undoped control, introducing either Ni or Ti defect levels resulted in an increase in f_{asym} at higher fields, but a slight decrease at low fields due to charge induced band bending. Ni doped devices also demonstrated a slight increase in breakdown field strength. Additional results will be presented at the meeting including capacitance-voltage measurements. This work shows that ALD can be an effective tool for engineering device behavior.

1. Alimardani et al. Appl. Phys. Lett. **102**, 143501 (2013)
2. Alimardani et al. Appl. Phys. Lett. **105**, 082902 (2014).
3. Holden et al. J. Appl. Phys. **129**, 144502 (2021).
4. Ichimura, *J. Electron. Mat.* **48**, 583 (2019).

3:20pm EM-WeA-4 Silicon-Doped Titanium Nitride with Near-Zero Temperature Coefficient of Resistivity (0.05 ppm/K) in the Temperature Range, 80 K - 420 K, S. Novia Berriel, C. Feit, University of Central Florida; M. Islam, University of Virginia; J. Shi, University of Central Florida; A. Dhamdhere, H. Kim, Eugenius, Inc.; P. Hopkins, University of Virginia; D. Le, T. Rahman, P. Banerjee, University of Central Florida

We demonstrate a materials system where the temperature coefficient of resistivity (TCR) can be effectively “dialed” to near zero (~ 0.05 ppm/K) across a wide temperature range spanning from 80 K to 420 K. Materials that show this behavior are referred to as near-zero temperature coefficient of resistivity (nz-TCR) materials. nz-TCR materials are instrumental for applications such as wearable strain sensors, automobile electronics, and microelectronics.

Our strategy to achieve nz-TCR is to atomically combine materials of opposing TCR's. Metals exhibit positive TCR, while semiconductors and insulators exhibit negative TCR. Atomic layer deposition (ALD) is well-suited for the task of tuning composition between metallic and insulating phases. To this end, we fabricate $Ti_{100-x}Si_xN$ thin films *via* ALD where the TiN (metal) and Si_3N_4 (insulating) are varied systematically across various sample sets. The TCR accordingly varies from positive (metallic and TiN rich) to negative (insulating and Si_3N_4 rich).

$Ti_xSi_{100-x}N$ films are deposited on a Eugenius® 300 mm commercial QXP mini-batch system. The ratio of precursor pulses are varied from $TiCl_4$ and dichlorosilane (DCS), with NH_3 as a co-reactant as described in our previous work¹. Specifically, Si content is varied for this work between $2.0 \leq x \leq 3.9$ at%. All $Ti_{100-x}Si_xN$ films are ~ 140 nm thick. The films are investigated *via* temperature-dependent van der Pauw and temperature-dependent Hall measurements, thermal conductivity measurements, x-ray diffraction, x-ray photoelectron spectroscopy, high-resolution transmission electron microscopy combined with electron energy loss spectroscopy.

Our results indicate the films are nanocrystalline in nature with Si segregating at the grain boundaries. The Si appears to “getter” residual oxygen. Supported by density functional theory (DFT) calculations, we show a loss in electron mean free path upon Si addition to TiN. The electron mean free path is approximately \sim lattice parameter for TiN thus, satisfying the Mooij rule² – a universal basic criteria for establish nz-TCR behavior in materials.

1.C. Feit, S. Chugh, A. R. Dhamdhere, H. Y. Kim, S. Dabas, S. J. Rath, N. Mukherjee and P. Banerjee, *Journal of Vacuum Science & Technology A* **38**, 062404 (2020).

2.J. H. Mooij, *physica status solidi (a)* **17**, 521-530 (1973).

4:20pm EM-WeA-7 An Auric Goldfinger Inspired Search for Copper Replacement Conductors, Sean King, Intel Corporation INVITED

In the spy film “Goldfinger”, MI6 agent James Bond’s nemesis Auric Goldfinger plotted to corner the world gold market by radioactively contaminating Fort Knox’s gold bullion supply. This presentation will examine the inverse scenario where present-day geopolitical tensions and supply chain constraints have the potential to limit the semiconductor

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industry’s ability to implement platinum group metals as potential copper conductor replacements. We will begin by first describing the interconnect resistivity scaling challenges that motivate the consideration of non-copper conductors and how certain platinum group metals offer the potential to outperform copper at nanometer wire dimensions (specifically Ruthenium, Iridium, and Rhodium). To further motivate consideration of platinum group metal conductors, we share a benchmarking Meta-analysis of thin film and nanowire resistivities reported in the scientific literature for these metals along with numerous other metals also in consideration (i.e. Cobalt, Tungsten, Molybdenum). We will conclude by examining the supply chain challenges that may ultimately play a role in the selection of future copper replacement conductors and discuss research needed to address these challenges.

5:00pm EM-WeA-9 Chalcogenide p-Type Transparent Conductors, Andriy Zakutayev, 15013 Denver W pkwy INVITED

Transparent conductors (TCs) are unusual materials that are optically transparent to visible light like insulating glass yet have electrical conductivity like opaque metals. The TCs are useful for a broad range of applications including flat panel displays, light-emitting diodes, solar cells, Particularly rare but useful for optoelectronic energy conversion devices are transparent materials that have p-type electrical conductivity with holes rather than electrons (n-type) as majority charge carriers. In contrast to n-type TCs that are usually oxides, some of the top performing p-type TCs are nitrides (e.g. Mg:GaN) or chalcogenides (i.e. sulfides, selenides, tellurides).

In this presentation, I will focus on wide band gap chalcogenide materials as p-type transparent conductors for photovoltaic and photoelectrochemical solar cells. First, I will give an overview desired physical properties of TCs besides transparency and conductivity, and present high-throughput research workshop that can be used to experimentally and theoretically screen candidate materials for TC applications [1]. Then I will give two examples of how these design principles and research methods can be used to synthesize and characterize $Zn_{1-x}Cu_xS$ [2] and $ZnTe_{1-x}Se_x$ [3] chalcogenide p-type transparent conductors, and integrate them in CdTe thin film photovoltaic devices [4].

[1] Chem. Rev. 2020, 120, 4007; [2] Matter 1 862 (2019); [3] J. Mater. Chem. C, 10, 15806 (2022); [4] ACS Applied Energy Materials 3 5427 (2020)

5:40pm EM-WeA-11 Strain Manipulation of Ferroelectricity and Flexoelectricity, Harold Hwang, Stanford University and SLAC National Accelerator Laboratory INVITED

The ability to create and manipulate materials in two-dimensional form has repeatedly had transformative impact on science and technology. We have developed a general method to create freestanding complex oxide membranes and heterostructures using epitaxial water-soluble buffer layers, with millimeter-scale lateral dimensions and nanometer-scale thickness. This facilitates many new opportunities we are beginning to explore; here we will focus on the use of tensile strain and strain gradients to control the ferroelectric and flexoelectric response of oxide membranes.

Applied Surface Science Division

Room B117-119 - Session AS+CA+EL+EM+SE+SS+TF-ThM

Quantitative Surface Analysis II

Moderators: Samantha Rosenberg, Lockheed Martin, Thierry Conard, IMEC, Belgium, Benjamen Reed, National Physical Laboratory, UK

8:00am **AS+CA+EL+EM+SE+SS+TF-ThM-1 OrbiSIMS: Signal, Noise and Transmission Are Three Sides of a Metrology Triangle**, G. Trindade, Y. Zhou, A. Eyres, National Physical Laboratory, UK; M. Keenan, Independent; Ian Gilmore, National Physical Laboratory, UK

In metrology, the science of measurement, a “metrology triangle” approach is used to provide a secure foundation. For example, the Quantum Metrology Triangle links Voltage, Resistance and Current through the Josephson Effect and the Quantum Hall Effect.

The OrbiSIMS¹, introduced in 2017, has become increasingly popular for biological and material sciences studies owing to its ability to give high confidence in molecular identification (mass resolving power > 240,000 and mass accuracy < 2 ppm) simultaneously with high confidence in localisation (micrometre scale spatially and nanoscale in depth). With a growing number of instruments internationally there is an increased need for metrology for reproducible measurements. We will show how Signal, Noise and Transmission form three sides of a metrology triangle that combine to enable better measurement. In a recent comprehensive study of the noise in an Orbitrap mass spectrometer, a probabilistic model was developed.² A region of the intensity scale is described by Poisson statistics allowing the scaling parameter, A, that relates ion current to the number of ions in the trap to be determined. A true signal intensity scale is then established which allows the useful yield of atoms in an implant layer to be measured. Through comparison with time-of-flight and magnetic sector instruments the fractional ion transmission is determined.³ We will discuss how Signal and Transmission combine to understand matrix effects in biological sample preparation and how understanding Signal and Noise are important for data analytical methods.

1. M. K. Passarelli. et al, I. S. Gilmore, Nat. Methods, 14(2017)12, 1175-1183.
2. M R. Keenan, G. F. Trindade, A. PirkI, C. L. Newell, K. Ayzikov, J. Zhang, L. Matjajic, H. Arlinghaus, A. Eyres, R. Havelund, J. Bunch, A. P. Gould, A. Makarov and Ian S. Gilmore, in preparation.
3. Y. Zhou, A. Franquet, V. Spampinato, G. F. Trindade, P. van der Heide, W. Vandervorst and I S Gilmore, in preparation.

8:20am **AS+CA+EL+EM+SE+SS+TF-ThM-2 Contribution of Imaging X-Ray Photoelectron Spectroscopy to Characterize Chrome Free Passivation Nano-Layer Deposited on Food-Packaging Tinplate: Composition and Chemical Environment**, E. Ros, Vincent Fernandez, CNRS, France; N. Fairley, CASAXPS, UK; B. Humbert, M. Caldes, CNRS, France

To protect metal from corrosion, passivation layer are widely used in food-packaging industry. Those Nano-metric protections create a thin oxide Nano-layer on the metal surface, making it less oxidisable. Common passivation are composed by chromium oxide[1], using hexavalent chromium as a reagent and reducing it. However, because of the toxicity of Cr(VI), European Union is gradually forbidding.Chromium Free Passivation Alternative is based on transitions metal oxides (Sn, Ti, Zr, Mn) and polymers. These samples present some roughness in few micron range observed by Atomic Force Microscopy.XPS Imaging were perform at different binding energy to allow extracting spectrum in each pixel over the eight (Mn 2p, O 1s, Sn 3d, Ti 2p,N 1s, C 1s, P 2s and Zr 3d) XPS core level process. This study show an anti-correlation between atomic concentration of Titanium and Tin Fig(1). We observe a ratio Sn oxide Sn metal homogeneous and independent of the Ti, Sn ratio More over using the vector method [2], [3] concurrently to height XPS core, we could extract two different chemical environments spectrum. The linear Least Square combination of these 2 spectrum allow us to model 131072 regions. To extract information form XPS data on heterogenous sample the combination of XPS imaging energy scan measurement with the vector method is a promising way. These results bring the useful information about different thin layer deposition steps. Imagerie XPS results are in agreement with Raman imagerie analysis

[1]R. Sandenbergh, M. Biermann, and T. von Moltke, ‘Surface Analytical Characterization of Chromium Passivation on Tinplate’, in *Passivation of Metals and Semiconductors, and Properties of Thin Oxide Layers*, P. Marcus and V. Maurice, Eds., Amsterdam: Elsevier Science, 2006, pp. 143–148. doi: 10.1016/B978-0-444-52224-5/50024-X.

[2]J. Baltrusaitis *et al.*, ‘Generalized molybdenum oxide surface chemical state XPS determination via informed amorphous sample model’, *Applied Surface Science*, vol. 326, pp. 151–161, Jan. 2015, doi: 10.1016/j.apsusc.2014.11.077.

[3]M. d’Halluin *et al.*, ‘Graphite-supported ultra-small copper nanoparticles – Preparation, characterization and catalysis applications’, *Carbon*, vol. 93, pp. 974–983, Nov. 2015, doi: 10.1016/j.carbon.2015.06.017.

8:40am **AS+CA+EL+EM+SE+SS+TF-ThM-3 Cryo-Xps for Surface Characterisation of Nanomedicines**, David Cant, National Physical Laboratory,, UK; Y. Pei, National Physical Laboratory, UK; A. Shchukarev, M. Ramstedt, University of Umea, Sweden; S. Marques, M. Segundo, University of Porto, Portugal; J. Parot, A. Molska, S. Borgos, SINTEF, Norway; C. Minelli, A. Shard, National Physical Laboratory, UK

Nanomedicines are an area of great interest for current and future pharmaceutical development. The use of nanoparticles to act as carriers for a therapeutic load has the potential to significantly improve medical outcomes, for example by allowing a therapeutic agent to circulate within the body for longer, or by allowing targeted delivery of a drug to a specific site. Such nanomedicines often rely on specific functional coatings to achieve their desired impact; for example the majority of nanomedicines currently available on the market utilise a poly-ethylene glycol (PEG) surface coating for its ‘stealth’ properties, helping nanomedicines evade the body’s clearance mechanisms. Accurate measurement of the surfaces of such nanomaterials is therefore of great importance, yet direct, quantitative surface chemistry measurements are not commonly available, and vacuum-based analysis methods such as XPS are unlikely to provide a representative measurement of the particles in their hydrated state.

Here we present to the best of our knowledge the first use of Cryo-XPS to provide direct, quantitative measurements of the surface chemistry of nanomedicines in a hydrated state. Two nanomedicine systems were measured: a drug-carrying polymer nanoparticle; and an mRNA loaded lipid nanoparticle. Both systems possessed a supposedly PEG-terminated surface, and were measured using XPS in both aqueous cryogenic state, and dry drop-cast onto a substrate. The results of these measurements clearly demonstrate that while the PEG surface cannot readily be observed in the dry state, the cryogenic measurements exhibit spectra that are consistent with the particle being measured in a hydrated condition.

9:00am **AS+CA+EL+EM+SE+SS+TF-ThM-4 Redox XPS as a Means to Address Some XPS Reproducibility Challenges**, Peter Cumpson, University of New South Wales, Australia

The challenge of better understanding of increasingly-complex specimens in surface analysis has been highlighted recently[1,2,3,4]. Especially at a time of high throughput XPS instruments and broadening of the (non-specialist) user community. An AVS survey conducted in 2018 found that 65% of those responding identified reproducibility as a significant issue [5].

There is an analogy to be made with some radically-different technologies. Machine Learning makes more sense of a moving image than a single snapshot, even if the snapshot were to come from a larger, better calibrated camera. Yet somehow we expect greater calibration precision, reference data and rigorous procedures to be the only route to reliable understanding of single spectra.

Generating a sequence of spectra from a progressively chemically-modified surface can remove many ambiguities that can otherwise cause misinterpretation. Such sequences thereby help with rapid understanding of the unmodified surface. On the theme of “Two is Better than One: Breaking Barriers with Coupled Phenomena” we present results from coupled stepwise oxidation/reduction of the surface and XPS to resolve such ambiguities for a wide range of materials and problems. Gas-phase oxidation agents are used to move through the redox states of a specimen in a controllable way, taking advantage of the logarithmic growth of oxide thickness. What is more, this oxidation is easy to implement in the entry-locks of modern XPS instruments through the use of vacuum ultraviolet light (VUV) and the *in situ* generation of ozone and gas-phase hydroxide free radicals. In the past there have been many studies of how particular materials react to ozone exposure at their surfaces, often employing XPS. Here we reverse this, and use ozone (and VUV) exposure to simplify the

interpretation of spectra from a wide range of unknown materials, we think for the first time.

[1] D R Baer et al, J. Vac. Sci. Technol. A 39, 021601 (2021); <https://doi.org/10.1116/6.0000873>

[2] G. H. Major et al, J. Vac. Sci. Technol. A 38, 061204 (2020); <https://doi.org/10.1116/6.0000685>

[3] G. H. Major et al, J. Vac. Sci. Technol. A 38, 061203 (2020) <https://doi.org/10.1116/6.0000377>

[4] D R Baer and M. H. Engelhard, Journal of Surface Analysis Vol. 26, No.2 (2019) pp. 94-95.

[5] D R Baer, J F Watts, A Herrera-Gomez, K J Gaskell, Surf Interface Anal. 2023; 1- 9. doi:10.1002/sia.7194

9:20am **AS+CA+EL+EM+SE+SS+TF-ThM-5 Sub-Nanometer Depth Profiling of Native Metal Oxide Layers Within Single Lab-XPS Spectra**, *Martin Wortmann*, N. Frese, Bielefeld University, Germany; K. Viertel, Bielefeld University of Applied Sciences and Arts, Germany; D. Graulich, M. Westphal, T. Kuschel, Bielefeld University, Germany

Many metals form nanometer-thin self-passivating native oxide layers upon exposure to the atmosphere, which affect their interfacial properties and corrosion behavior. Such oxide layers are commonly analyzed by X-ray photoelectron spectroscopy (XPS). Here we propose a simple and accessible depth profiling approach for oxide layers with sub-nanometer depth resolution from single lab-XPS spectra. Metals and their oxides can be distinguished by a binding energy shift to quantify their distinct signal contributions. Analogous to the widely used Hill equation we utilize the known photoelectron's inelastic mean free path to calculate the characteristic oxide layer thickness. However, in contrast to the Hill equation we analyze not only one, but all orbital energies in the XPS spectrum to develop a model that accounts for a depth-resolved concentration profile at the oxide-metal interface. The proposed model not only improves the accuracy and reproducibility of earlier methods but also paves the way for a more holistic understanding of the XPS spectrum.

9:40am **AS+CA+EL+EM+SE+SS+TF-ThM-6 A Tag-and-Count Methodology Based on Atomic Layer Deposition (ALD) and Low Energy Ion Scattering (LEIS) for Quantifying the Number of Silanols on Fused Silica**, *Josh Pinder*, Brigham Young University

The concentration of surface silanols governs many of the properties of glass and fused silica surfaces including surface wetting, surface contamination rates, and thin film adhesion. Indeed, the concentration of surface silanols is impactful for diverse fields such as atomic layer deposition (ALD), chromatography, catalysis, and displays. Accordingly, various analytical and theoretical methods have been employed to determine the number of silanols on surfaces, including density functional theory, FTIR, thermogravimetric analysis, and temperature programmed desorption mass spectrometry. However, many of these methods are better applied to particulate materials than surfaces. In this presentation, we discuss a method for directly

measuring the concentrations of surface silanols on silica-containing surfaces via a tag-and-count methodology. This approach is based on tagging surface silanols by ALD via a single pulse of dimethylzinc or diethylzinc and then quantifying the number of tags (zinc atoms) using high

sensitivity-low energy ion scattering (HS-LEIS). Our method yielded the literature value for both fully hydroxylated fused silica and also fused silica that had been heated to 500, 700, and 900 C. We see this capability as enabling for all who work with glass, fused silica, and silicon wafers,

including for ALD.

11:00am **AS+CA+EL+EM+SE+SS+TF-ThM-10 ASSD Peter M. A. Sherwood Mid-Career Professional Awardee Talk: Providing Fundamental Mechanistic Insights Into Single-Site Catalytic Reactions**, *Jean-Sabin McEwen*¹, Washington State University **INVITED**

The single atom limit achieves the ultimate degree of material efficiency for supported metal catalysts. To this end, the ability to create highly dispersed, single-site catalysts, which are highly efficient and have low cost, is very much desirable. While single atom sites can be created, there is still disagreement over whether the single atom sites are indeed catalytically active or if the observed catalytic activity of single-site catalysts is due to metal nanoparticles either unobserved during initial microscopy studies or formed upon exposure to catalytic conditions. Such disagreements create a crucial need for the development of well-defined single-site catalysts with an accurate theoretical model in order to correctly determine the chemical nature of the catalytically active sites. To this end, we provide new atomistic insights regarding the "44" Cu surface oxide through the integration of synchrotron-based X-ray Photoelectron Spectroscopy (XPS) measurements, Synchrotron X-ray Diffraction measurements (SXRD), Scanning Tunneling Microscopy (STM) and Density Functional Theory (DFT) techniques. We also quantify the low-temperature CO oxidation kinetics on Pt single-site catalysts supported on the "29" Cu surface oxide. The "29" Cu surface oxide is a high coverage chiral structure that arises when we further oxidize the "44" structure. Using STM, CO temperature programmed desorption (TPD), and DFT techniques, we determine that an accurate model for the "29" Cu oxide surface is formed from the growth of a Cu_xO layer formed from 6 fused hexagonal rings above the Cu (111) surface where 5 oxygen adatoms are added at the center of the Cu_xO rings. Furthermore, we determine the state of the Pt single atoms before, during, and after reaction through a combination of theoretical and experimental techniques. We also correlate ambient pressure experiments, surface science measurements and first principles-based calculations to demonstrate that Pt/Cu(111) single-atom alloys (SAAs) oxidized with varying degrees of O₂ exposure can be reduced with H₂ with reasonable kinetics (hours). This is in contrast to oxidized pure Cu(111) where such reduction is very slow (days). We further contrast the catalytic properties of Rh/Cu(111) SAAs with varying degrees of O₂ exposure to the those of Pt/Cu(111) SAAs. Finally, we report the effects of a copper oxide thin film toward the segregation of noble metal single-atoms on Cu (111) using DFT.

11:40am **AS+CA+EL+EM+SE+SS+TF-ThM-12 Beyond the Physical Origin of the Shirley Background in Photoemission Spectra: Other Predictions of the Interchannel Coupling with Valence Band Losses Mechanism**, *Alberto Herrera-Gomez*, CINVESTAV-Unidad Queretaro, Mexico

The physical mechanism proposed in our 2017 paper about the origin of the Shirley background in photoemission spectra¹ es based on interchannel coupling² but with the important addition of energy losses in the valence band.³ Besides the Shirley background, it is possible to derive other predictions of the interchannel Coupling with Valence Band Losses mechanism (ICLM). Two of them are discussed in this paper: 1) the quantitative relation between Auger peaks and the Shirley background and 2) the conduction-band-like structure of the extended region of the Shirley background.

¹ A. Herrera-Gomez et al. Surface and Interface Analysis 50(2), 246–252 (2018).

² E.W.B. Dias et al. Phys Rev B 78(2), 4553–4556 (1997).

³

<http://www.qro.cinvestav.mx/~aherrera/reportesInternos/unknownOriginShirley.pdf>

12:00pm **AS+CA+EL+EM+SE+SS+TF-ThM-13 Aging of Hydrophilicity in a Nano-Textured SS316 Thin Film Fabricated by Magnetron Sputtering**, *Pakman Yiu*, Ming Chi University of Technology, Taiwan; *J. Chu, J. You*, National Taiwan University of Science and Technology, Taiwan

According to the structural zone model by J.A. Thronton[1], we may manipulate the surface morphology of a thin film by altering the deposition temperature and vacuum. Therefore in this study, we prepared a series of SS316 thin film by magnetron sputtering under different Argon working pressure. Resultant thin film possessed a pressure dependent nano-textured surface which was dependent on working pressure. Furthermore, we discovered that the textured surface was highly hydrophilic (water

¹ ASSD Peter Sherwood Award

contact angle <15 degrees). The hydrophilicity could be attributed to the combinatorial contribution of surface roughness and capillary effect. However, we also discovered that the hydrophilicity aged with time, where after 21 days the surface turned hydrophobic with water contact angle >90 degrees. XPS studies on both as-deposited and 21-days stored sample films revealed that there was a Carbon-rich surface layer on the surface which grew with time. Interestingly when we tried to clean the surface with Argon atmospheric plasma, the hydrophilicity was almost fully restored. Results revealed that the aging of hydrophilicity may due to the fact that nano-surface texture gathers hydrocarbons in the atmosphere, which eventually formed an extra film that altered the surface wetting property. Understanding the aging mechanism and method of recovery may contribute to the development of a long-lasting hydrophilic surface, which is very useful in applications such as self-cleaning surface and medical apparatus[2,3]

[1] J.A. Thornton, *Ann. Rev. Mater. Sci.* 7 (1977) 239–260.

[2] A. Syafiq, B. Vengadaesvaran, A.K. Pandey, Nasrudin Abd. Rahim, J. *Nanomater.* 2018 (2018) 6412601.

[3] M. Xiao, Y.M. Chen, M.N. Biao, X.D. Zhang, B.C. Yang, *Mater. Biol. Appl.* 70 (2017) 1057–1070.

Electronic Materials and Photonics Division Room B116 - Session EM+TF-ThM

Wide- and Ultra-Wide Band Gap Materials and Devices

Moderators: Erica Douglas, Sandia National Laboratories, Seth King, University of Wisconsin - La Crosse, Daniel Pennachio, Naval Research Laboratory

8:00am **EM+TF-ThM-1 Ga₂O₃ and AlN for Power and RF Electronics, Grace Xing**, Cornell University **INVTED**

It's of little surprise that there has been a consistent drive toward the use of wider bandgap materials for power and RF electronics. After all, the wider the bandgap, the greater the breakdown field, opening the door to making devices with a higher breakdown voltage for the same material thickness. Furthermore, the saturation velocity of mobile carriers in ultra-scaled devices tends to be about $1-2 \times 10^7$ cm/s in most semiconductors.

However, nature is not always that generous. Typically, a move to a wider bandgap is accompanied by more challenging doping, point defect control, ohmic contacts, quality junctions, along with difficulty in making high-quality native substrates. Ga₂O₃ and AlN are among the promising contenders, given their large bandgaps, availability of large-size bulk substrates (>2 inches), and heterojunctions. But both lack p-type. AlN possesses high thermal conductivity – slightly worse than that of copper but Ga₂O₃ has a low thermal conductivity – worse than that of sapphire.

Given all these promises and obstacles, is it possible to harvest all the benefits in AlN and Ga₂O₃ and demonstrate devices that are superior to those made from SiC and GaN? I will reflect on our efforts in seeking answers to these questions in the past many years researching on power and RF devices with a focus on Ga₂O₃ and AlN [1-6].

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[4] A. Green *et al.*, *APL Materials* (2022) Beta-gallium oxide power electronics.

[5] E.K. Kim *et al.*, *APL* (2023) N-polar GaN/AlGaIn/AlN HEMTs on single-crystal bulk AlN substrates.

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8:40am **EM+TF-ThM-3 Deep UV Photoluminescence Mapping of Gallium Oxide, Matthew McCluskey**, Washington State University

Photoluminescence (PL) spectroscopy is an important method to characterize dopants and defects in gallium oxide. Features in the PL spectrum include the intrinsic UV band, blue and green bands that involve donor-acceptor pairs, and red emission due to Cr³⁺ impurities. PL mapping with excitation wavelengths as short as 266 nm reveals the spatial distribution of these features with submicron resolution. In Czochralski-grown β-Ga₂O₃:Fe, the Cr³⁺ emission intensity shows striations that are attributed due to inhomogeneities during growth. In addition to defects in the bulk, PL microscopy has revealed several specific defects on the surface. Some of these localized centers are very bright UV emitters. Raman scans of these bright emitters revealed hydrocarbon peaks, which may point toward the origin of the light emission. Samples damaged by high-intensity laser pulses show significant changes in the intensity and energy of the intrinsic UV band.

9:00am **EM+TF-ThM-4 Spatially Resolved Polymorph Conversion in Ga₂O₃, U. Bektas, P. Chekhonin, R. Heller, R. Hübner, M. Liedke, N. Klingner, Gregor Hlawacek**, Helmholtz Zentrum Dresden-Rossendorf, Germany

Monoclinic galliumoxide (β-Ga₂O₃) is a promising wideband gap semiconductor with a bandgap of 4.7 eV and a high breakdown voltage. However, the existence of several metastable polymorphs and the immature fabrication technology limits its applications. The research is based on the recent observation that β-Ga₂O₃ can reliably be converted into γ-Ga₂O₃ using high energy ion beams [1,2]. It could also be shown that the resulting γ-Ga₂O₃ layer exhibits an exceptional tolerance towards high fluence ion beam irradiation [3].

Here, we use focused ion beam (FIB) induced processing to convert β-Ga₂O₃ into γ-Ga₂O₃ in a spatially controlled way. We employ focused Ne ions from a helium ion microscope (HIM) and liquid metal alloy ion sources (LMAIS) based FIB with Co, Si, and In to induce the polymorph conversion. Electron backscatter diffraction (EBSD), transmission electron microscopy (TEM) and atomic force microscopy (AFM) are used to confirm, in a spatially resolved way, the successful polymorph conversion. From the obtained EBSD data the orientation relationship between the irradiated and unirradiated material is resolved. Broadbeam irradiated reference samples have been used to corroborate these results with channeling Rutherford backscattering spectrometry (c-RBS), X-ray diffraction (XRD) and Doppler broadening variable energy positron annihilation spectroscopy (DB-VEPAS) results. The obtained crystal structure and defect distribution data supports the model suggested for the conversion mechanism [3].

This research is supported by the tax funds on the basis of the budget passed by the Saxonian state parliament in Germany and the COST Action CA19140 FIT4NANO <https://www.fit4nano.eu/>.

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[2] J. Garcia-Fernandez, S.B. Kjeldby, Formation of γ-Ga₂O₃ by ion implantation: Polymorphic phase transformation of β-Ga₂O₃, *Appl. Phys. Lett.* 121 (2022), 191601.

[3] A. Azarov, J. G. Fernández, J. Zhao, F. Djurabekova, H. He, R. He, Ø. Prytz, L. Vines, U. Bektas, P. Chekhonin, N. Klingner, G. Hlawacek, A. Kuznetsov, Universal radiation tolerant semiconductor (2023), doi:10.48550/ARXIV.2303.13114.

9:20am **EM+TF-ThM-5 Low-Temperature Epitaxy and in-situ Doping of Ultrawide Bandgap Ga₂O₃ Films via Hollow-Cathode Plasma-ALD, S. Ilhom, A. Mohammad, N. Ibrahimli, J. Grasso, B. Willis**, University of Connecticut; A. Okyay, OkyayTech Inc; **Necmi Biyikli**, University of Connecticut

Wide and ultrawide bandgap (WBG/UWBG) semiconductors make the backbone of high-power high-frequency electronics, used in electric vehicles, 5G and beyond wireless communication systems, and smart power grids. Gallium oxide (Ga₂O₃) is an emerging UWBG semiconductor showing superior material properties particularly ideal for harsh environments (high temperature, high-energy radiation, corrosion) applications. Reducing the growth and doping process temperatures for Ga₂O₃ would potentially enable a wider integration platform towards post-CMOS integration and flexible electronics.

Herein, we report on the low-temperature as-grown crystalline β-Ga₂O₃ films on Si, glass, and sapphire via hollow-cathode plasma-assisted atomic layer deposition (HCP-ALD). The films were deposited using triethylgallium (TEG) and Ar/O₂ plasma as metal precursor and oxygen co-reactant, respectively. Additionally, we have employed *in situ* atomic layer doping to n-type dope Ga₂O₃ films where tris-dimethylaminosilane

(TDMAS) and tetrakis-dimethylaminotin(IV) (TDMASn) were utilized as the dopant precursors. Growth experiments have been performed at 240 °C under 50 W rf-plasma power. The doping process was carried out via both supercycle (ABC-type ALD-cycle) and co-dosing methods. Additionally, each unit ALD-cycle was followed by an *in-situ* Ar-plasma annealing treatment, which consisted of Ar-plasma exposure for 20 seconds at 250 W rf-power. Both *in-situ* and *ex-situ* ellipsometry were employed to measure the thickness and optical properties of the Ga₂O₃ samples. X-ray diffraction (XRD) of the sample on sapphire revealed epitaxial Ga₂O₃ films with monoclinic *b*-phase, while GIXRD analyses of the samples grown on Si and glass displayed *b*-phase polycrystalline films. HR-STEM imaging and EDX elemental analysis confirmed the epitaxial relationship of the films grown on sapphire substrates and displayed successful incorporation of dopant elements. Preliminary electrical conductivity measurements showed highly resistive samples. Therefore, *ex-situ* thermal annealing studies are carried out to explore dopant activation processes. Further studies from our XPS characterizations will provide additional insight about the chemical bonding states of the dopant species. A significant effort will be devoted for the comparison of Si and Sn-doping strategies and potential suggestions will be provided to overcome the challenges in achieving device quality undoped and doped Ga₂O₃ layers at low processing temperatures.

9:40am **EM+TF-ThM-6 Growth of Metastable Ga₂O₃ Epitaxial Films Using Metalorganic Chemical Vapor Deposition and Halide Vapor Phase Epitaxy, Jingyu Tang, K. Jiang, M. Weiler, M. Moneck, R. Davis, L. Porter, Carnegie Mellon University**

Gallium oxide (Ga₂O₃) is an ultra-wide bandgap semiconductor of interest for electronics that can operate in extreme conditions, such as high power, high temperature and radiation exposure. β-Ga₂O₃ is thermodynamically stable at atmospheric conditions up to its melting point and is the phase produced in melt-grown, single-crystal substrates. However, epitaxial films of metastable polymorphs of Ga₂O₃ are also of interest because they possess unique properties – such as piezoelectricity, ferroelectricity, or ferromagnetism – that could lead to new types of heterostructure devices. We report here the growth and characterization of both mixed-phase and phase-pure epitaxial films of each of the metastable polymorphs: κ(ε) and γ using metalorganic chemical vapor deposition (MOCVD); and α, κ and γ using halide vapor phase epitaxy (HVPE). The effect of variables, such as substrate temperature, will be reported, as will the use of different substrates / orientations to produce phase-pure epitaxial films of α-, κ-, and γ-Ga₂O₃ in the same grown runs. The microstructure, composition, and morphology of the films and film/substrate interfaces were characterized using x-ray diffraction (XRD) θ-2θ scans, rocking curves, and φ scans; scanning electron microscopy (SEM); and high-resolution cross-section transmission electron microscopy (TEM) with energy dispersive x-ray (EDX) analysis.

11:00am **EM+TF-ThM-10 AlGa_n/Ga_n HEMTs with Submicron Gates for High-Frequency Operation in Harsh Space Environments, Isabel Harrysson Rodrigues, M. Rais-Zadeh, Jet Propulsion Laboratory, California Institute of Technology**

Indium aluminum nitride/gallium nitride high electron mobility transistors (AlGa_n/Ga_n HEMTs) offer excellent properties such as high electron mobility and wide bandgap, making them ideal for high-frequency and high-power applications, in harsh environments. The wide band gap of the AlGa_n/Ga_n heterostructure infers inherent radiation tolerance compared to traditional Si microelectronics. Owing to the advantageous two-dimensional electron gas, AlGa_n/Ga_n HEMTs can provide increased sensitivity, fast response time, and low noise levels while withstanding extreme temperatures, radiation, and vibrations found in space. Its robustness and reliability make it ideal for long-term missions, ensuring accurate and uninterrupted sensing and detection in difficult space conditions. DC operation has been achieved for AlGa_n/Ga_n HEMTs with various larger gate dimensions. Separate studies have shown successful operation of AlGa_n/Ga_n HEMTs at high temperatures reaching 1000°C. However, in achieving high-frequency operation, the device geometry must be size-optimized from large-area to scaled gate lengths in the submicron regime. RF analysis at both room temperature and high temperature is a necessary next step to determine the merits of these devices for extreme environment applications where these devices have advantages over other semiconductor technologies. In this work, the performance of AlGa_n/Ga_n HEMTs are optimized by reducing the gate length toward high-frequency operation in harsh space environments, with specific applications in on-board rover communications and for in situ readout of sensor data. The geometry schemes were chosen during the design phase, and the microfabrication process, metallization, and passivation materials were

carefully evaluated. These results are promising for further testing, e.g., radiation tolerance, high temperatures, and monolithic circuit integration. The presented devices have an advantage over traditional heterogeneous integration strategies for GaN devices which requires silicon ASICs that, without cooling, cannot operate in high-temperature environments.

11:20am **EM+TF-ThM-11 Selected-Area P-Type Doping of GaN Using Focused-Ion Beams, Sam Frisone, University of Michigan; M. Titze, A. Katzenmeyer, Sandia National Lab; B. Li, Yale University; A. Flores, Sandia National Lab; Y. Wang, Los Alamos National Laboratory; R. Goldman, University of Michigan; E. Biejelec, Sandia National Lab; J. Han, Yale University**

Due to their potential for high breakdown voltage and low on-resistance, GaN-based electronic devices are promising for high-power and high-frequency electronics. Vertical GaN p-i-n devices are expected to offer improved thermal management and reduced leakage current in comparison to their lateral counterparts; however, typical etching and regrowth processes introduce interfacial impurities that limit control of dopant profiles. Thus, a strategy for both vertical and lateral dopant selectivity, without the need for etching and regrowth, is essential for the development of high-quality vertical GaN devices. Here, we report on Mg doping using a liquid-metal ion source (LMIS) in a mass-selecting focused-ion-beam (FIB) column. For these studies, an unintentionally doped (UID) 3.6μm GaN layer is grown by metalorganic chemical vapor deposition on n-type GaN. In preparation for FIB implantation, the UID GaN layer was patterned with an array of Au/Ti markers. Checkerboard patterns consisting of alternating 70x70 and 50x50μm squares, with and without Mg FIB implantation, were prepared using a Mg-doped AuSi eutectic as the LMIS. The ion energies were set to 70keV, resulting in a most probable ion implantation depth of 70nm; seven ion fluences ranging from 10¹²-10¹⁵ cm⁻², corresponding to Mg concentrations of 10¹⁶-10¹⁹ cm⁻³, were used. To examine the activation of Mg dopants in GaN, we compare the pristine and implanted regions before and after rapid-thermal processing (RTP). A distinct checkerboard pattern is observed in secondary electron (SE) images, with reduced SE image intensities in the implanted regions compared to the pristine regions. Following removal of the Au/Ti markers and 30 seconds of RTP at 1100°C, the checkerboard pattern is reduced in the vicinity of the four lowest ion fluences. For all regions, cathodoluminescence (CL) spectroscopy reveals GaN near-band edge (NBE) emissions at 3.4eV. The intensity of NBE emission is highest in the pristine regions, especially those in the vicinity of the two lowest ion fluences. Furthermore, in pristine regions adjacent to the two lowest ion fluences we observe CL emissions at 2.85eV and 2.2eV. As discussed in [1], we attribute these emissions to impurity-related donor-acceptor pairs and yellow luminescence, respectively. The reduced SE image intensity and limited CL emission in the vicinity of the highest ion fluences suggest incomplete Mg dopant activation. The influence of additional RTP on the dopant activation will be discussed. [1] 10.1016/j.nanoen.2022.107689

11:40am **EM+TF-ThM-12 Epitaxial Growth and Characterization of High ScN Fraction ScAlN on NbN and SiC, Matthew Hardy, S. Katzer, A. Lang, E. Jin, N. Nepal, B. Downey, V. Gokhale, V. Wheeler, U.S. Naval Research Laboratory**

ScAlN thin films have attracted significant attention due to their factor of five increase in piezoresponse over AlN for Sc_{0.43}Al_{0.57}N. Integration of metallic epitaxial NbN with ScAlN using molecular beam epitaxy (MBE) enables a pathway towards a highly conductive lower electrode while preserving high crystal quality even in relatively thin ScAlN films suitable for use at or above X-band frequencies. Maintaining phase-pure and high crystal quality Sc_xAl_{1-x}N at high x is critical to improve resonator bandwidth and reduce insertion loss.

In this work, we show the importance of the ScAlN nucleation layer to the final crystal quality and anomalously oriented grain (AOG) density of MBE-grown ScAlN films on SiC and NbN/SiC. Starting the ScAlN growth with a Sc_{0.32}Al_{0.68}N layer can suppress the rock-salt ScAlN material at the nucleation interface, as seen by reflection high-energy electron diffraction (RHEED) and transmission electron diffraction (TEM). Nucleation using a linear composition grade from Sc_{0.32}Al_{0.68}N to Sc_{0.40}Al_{0.60}N over 100 nm leads to further improvements in the RHEED pattern, including a narrowing of the spots early in the growth, as well as elimination of remaining ring-like character in the final RHEED pattern after an additional 40 nm of growth, resulting in an X-ray diffraction (XRD) FWHM as low as 1.22° for ScAlN films grown on SiC. TEM shows near elimination of cubic grains that otherwise form in the initial layers of the Sc_{0.40}Al_{0.60}N. The grade thickness can be

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reduced to 25 nm (with the remaining 125 nm $\text{Sc}_{0.40}\text{Al}_{0.60}\text{N}$) without degrading the XRD FWHM or RHEED pattern, increasing the average ScN fraction from 0.373 to 0.393. Finally, a 500-nm-total-thickness sample (100 nm $\text{Sc}_{0.32}\text{Al}_{0.68}\text{N} \rightarrow \text{Sc}_{0.40}\text{Al}_{0.60}\text{N}$, 400 nm $\text{Sc}_{0.40}\text{Al}_{0.60}\text{N}$) was grown to show the impact of defect annihilation in thicker films, resulting in a reduction of XRD FWHM to 0.89°. The improved layer initiation shows that more gradual changes in surface energy and strain reduces the nucleation of undesirable cubic grains, and may point to a general strategy for elimination of anomalous grains in high ScN fraction ScAlN.

Employing a similar growth approach and using a novel two-step AlN interlayer enables integration of ScAlN on an NbN epitaxial metal lower electrode. Growth conditions to first encapsulate the NbN layer, and then provide a smooth surface for ScAlN nucleation are critical to minimize degradation in XRD FWHM or AOG density. ScAlN on NbN structures enable characterization of the ScAlN dielectric constant and electromechanical coupling coefficient (k_t^2). A dielectric constant of 25 and k_t^2 of 27% was extracted for $\text{Sc}_{0.32}\text{Al}_{0.68}\text{N}$ from a $\text{Sc}_{0.32}\text{Al}_{0.68}\text{N}/\text{AlN}/\text{NbN}/\text{SiC}$ sample.

12:00pm **EM+TF-ThM-13 Novel Graphene and SiC Epitaxy to Enable Film Transfer**, *Daniel Pennachio, J. Hajzus, A. Lang*, US Naval Research Laboratory; *R. Stroud*, Former employee of US Naval Research Laboratory; *R. Myers-Ward*, US Naval Research Laboratory

Remote epitaxy (RE) is a promising technique for epitaxial film transfer that utilizes graphene as a release layer [1]. Graphene grown on SiC(0001) substrates through Si sublimation or through propane chemical vapor deposition (CVD) is an ideal platform for remote epitaxy of wide bandgap (WBG) semiconductors as there is no need for a graphene transfer step, mitigating contamination or defects that can complicate the remote epitaxy process. In addition, the graphene/SiC materials system is compatible with commercially-viable WBG semiconductor growth and processing, making it a suitable choice for scalable future development. A challenge to utilizing SiC is that CVD growth is typically conducted using high-temperature hydrogen-based chemistries that could damage or remove graphene. This study investigates the effect of alternative low- H_2 CVD growth conditions on SiC/graphene/SiC(0001) remote epitaxy that may reduce damage to the graphene barrier. In addition, graphene preparation and associated surface morphology is varied to explore its effect on SiC epilayer formation.

For this work, the effects of Ar: H_2 process gas flow ratio, growth precursor C/Si ratio, and growth temperature on hot-wall CVD SiC RE crystalline quality were investigated. Both semi-insulating nominally on-axis 6H-SiC(0001) and n-type 4° off-axis 4H-SiC(0001) substrates were used to produce different surface morphologies and graphene layer numbers. Nomarski optical microscopy, scanning electron microscopy, and atomic force microscopy found CVD deposition at 1620°C with Ar/ H_2 ratios <20/5 slm, and C/Si ratios <1.55 to have the smoothest surface morphology and fewest polytype inclusions. Substrates with offcuts <0.1° from SiC(0001) exhibited lower epilayer macrostep density but showed evidence of polytype impurities and 3D growth at C/Si ratios > 1.0. RE on EG/4H-SiC(0001) substrates with a 4° off-cut from SiC[0001] had a wider parameter range resulting in single-crystalline growth compared to growth on the nominally on-axis substrates despite growth of >1 monolayer EG on these substrates. This study found smooth, single-crystalline polytype-pure SiC(0001) epilayers on EG substrates could be grown using predominantly Ar carrier gas, with H_2 concentrations as low as ~2%. Through this study, optimal SiC RE growth conditions are suggested for a balance of EG survivability and SiC film morphology.

[1] Kim, Y., Cruz, S., Lee, K. et al. Nature 544, 340–343 (2017).

Electronic Materials and Photonics Division Room B116 - Session EM-ThA

Theme: CMOS+X: Piezoelectrics, Ferroelectrics, Multiferroics, and Memory

Moderators: M. David Henry, Sandia National Labs, **Stephen McDonnell**, University of Virginia

2:20pm **EM-ThA-1 Factors That Stabilize the Ferroelectric Phase of Hafnia**, **Jon Ihlefeld**, *S. Jaszewski, S. Fields, M. Lenox, B. Aronson*, University of Virginia; *T. Cai, B. Sheldon*, Brown University; *S. Calderon*, Carnegie Mellon University; *K. Kelley*, Oak Ridge National Laboratory; *T. Beechem*, Purdue University; *M. Henry*, Sandia National Laboratories; *E. Dickey*, Carnegie Mellon University

INVITED

Just over a decade ago, ferroelectricity – the presence of a permanent reorientable dipole – was reported in doped hafnium oxide thin films. This report generated a great deal of excitement as the inherent silicon compatibility of HfO_2 , coupled with the extreme thinness of the films that exhibited the ferroelectric response promised to overcome a number of technological hurdles limiting utilization of ferroelectrics in microelectronics. In spite of the great promise and significant worldwide research efforts, this material has not yet been mass deployed owing to a number of challenges. These include: 1) performance variability for nominally identical materials and devices produced by different research groups, 2) performance variability as films are used in devices – i.e. polarization changes with use. Virtually all of these issues can be traced to phase impurities in the films – i.e. the ferroelectric phase co-exists with non-ferroelectric phases. In this presentation, I will highlight our group's efforts to better understand this potentially game changing material and to overcome some of these challenges. Two major phase stabilizing mechanisms will be discussed, including: 1) oxygen vacancies, which in pure HfO_2 will be shown to exist in concentrations >20% and whose impact on phase stability appears to be greater than crystallite size and 2) mechanical stress, particularly the role of the top electrode, which serves as an out-of-plane rather than in-plane mechanical constraint. It will be shown that often-cited thermal expansion mismatch of the electrodes and hafnia layers is not consistent with the hafnia film stresses measured and is not a valid explanation of the so-called electrode capping effect. Finally, using synchrotron-based diffraction and spectroscopy, we will show how the phases evolve as the ferroelectric is poled and cycled and how this leads to performance instabilities. Finally, it will be shown that the presence of the non-ferroelectric tetragonal phase may be overstated and that an antipolar (e.g. truly antiferroelectric) orthorhombic phase with space group $Pbca$ is common in hafnium zirconium oxide films and can better explain the observed electrical, vibrational, and mechanical behaviors.

3:00pm **EM-ThA-3 Internal Photoemission (IPE) Spectroscopy Measurement of Interfacial Barrier Heights in Pristine and Poled Ferroelectric ALD Hafnium-Zirconium-Oxide Metal/Oxide/Semiconductor (MOS) Devices**, **Jessica Haglund**, Oregon State University; *T. Mimura*, Gakushuin University, Japan; *J. Ihlefeld*, University of Virginia; *J. Conley*, Oregon State University

Ferroelectric $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$ (HZO) has attracted much attention for non-volatile memory applications since HfO_2 is already used as a gate dielectric. For efficient integration, knowledge about how HZO interacts with electrode materials is necessary. IPE provides a method to observe interfacial energy barrier heights "in-situ" in working devices. We previously reported the barrier heights in as-deposited HZO in metal insulator metal structures (MIM) [2]. However, both post deposition/metallization annealing, "waking", and "poling" are necessary to stabilize and exploit the ferroelectric behavior [1]. To date, there have not been reports of IPE barrier measurement on woken and poled HZO in metal oxide semiconductor (MOS) structures.

In this study, atomic layer deposition was used to deposit 20 nm HZO on a degenerately doped p-Si using 102 supercycles of TDMAH (HfO_2) and TDMAZ (ZrO_2). Next, a blanket 20 nm TaN film was deposited and annealed for 30 seconds at 600°C. This TaN layer was then stripped and replaced by an optically transparent electrode of 5nm TaN and 5 nm Pd. Waking was done using a 5000 cycle 1 kHz square wave with magnitude +/- 5V. Once a device was woken, it was poled using a single voltage pulse of +4V. IPE measurements were done by focusing a single wavelength of light on the device surface while applying a voltage (V_{app}) between the Si and grounded top electrode and sweeping photon energy from 1.7 eV to 5.5 eV while

measuring IPE current. The measurement is repeated at 0.1V increments from -1.5 to 1.5 V. IPE current thresholds were extracted at each applied voltage, V_{app} , and plotted vs. $V_{\text{app}}^{1/2}$. This plot was extrapolated to zero voltage to obtain the band offsets between the TaN and the Si conduction band (CB) and valence band (VB) and the HZO VB.

For pristine devices the TaN, Si CB, and Si VB barriers were measured at 2.5 eV, 3.5 eV, and 4.4 eV, respectively. Following waking, the TaN barrier was reduced to 2.1 eV, possibly indicating redistribution of oxygen defects toward the TaN interface. The Si CB and VB remained roughly the same at 3.4 and 4.6eV, respectively. The barriers of positive poled devices were within error of the woken devices, but the negative poled devices showed an increase in the TaN barrier to 2.8 eV and a decrease in the Si CB and VB barriers to 3.1 and 4.4 eV respectively. This suggests oxygen vacancy movement away from the TaN interface. IPE measurements give new insight into HZO devices operation. C-V and I-V measurements will be discussed at conference.

[1]E. D. Grimley *et al.*, *AEM2* 1600173, (2016)

[2]M. A. Jenkins *et al.*, *ACS AMI* 13, 14634–14643, (2021)

3:20pm **EM-ThA-4 Phase Transformations Driving Biaxial Stress Reduction During Wake-Up of Hafnium Zirconium Oxide Thin Films**, **Samantha Jaszewski**, Sandia National Laboratories; *S. Fields*, University of Virginia; *S. Calderon*, Carnegie Mellon University; *B. Aronson*, University of Virginia; *T. Beechem*, Purdue University; *K. Kelley*, Oak Ridge National Laboratory; *E. Dickey*, Carnegie Mellon University; *J. Ihlefeld*, University of Virginia

Biaxial stress has been identified to play an important role in the stability of the ferroelectric phase in hafnium oxide-based thin films. However, thus far, the stress state during wake-up has not been quantified. In this work, the stress evolution with electric field cycling in hafnium zirconium oxide capacitors is evaluated. The remanent polarization of a 20 nm thick hafnium zirconium oxide thin film increases from 13.8 $\mu\text{C}/\text{cm}^2$ in the pristine state to 17.6 $\mu\text{C}/\text{cm}^2$ following 10^6 field cycles at 2.5 MV/cm. This increase in remanent polarization with field cycling is accompanied by a decrease in relative permittivity of approximately 1.5, which could indicate that a phase transformation has occurred. The presence of a phase transformation is confirmed by nano-Fourier transform infrared spectroscopy measurements that show an increase in the ferroelectric phase after wake-up. Using an X-ray diffractometer with a collimated source and a two-dimensional detector, diffraction patterns from individual devices electric field-cycled from 0 to 10^6 cycles are collected and stress quantified using the $\sin^2(\psi)$ technique. The biaxial stress was measured in several stages of wake-up and was observed to decrease from 4.3 ± 0.2 to 3.2 ± 0.3 GPa. This work provides new insight into the mechanisms associated with polarization wake-up in hafnium zirconium oxide.

3:40pm **EM-ThA-5 AVS Russell and Sigurd Varian Awardee Talk: Novel Chalcogenide Superlattice-Based Energy-Efficient Phase-Change Memory for 3D Heterogeneous Integration**, **Asir Intisar Khan¹**, *X. Wu, A. Daus, H. Kwon, K. Goodson, H. Wong, E. Pop*, Stanford University

Today's nanoelectronics are reaching limits of energy and speed with conventional materials and traditional layouts that separate logic and memory. For tackling this grand challenge, phase-change memory (PCM) holds promise for both digital memory and brain-inspired computing.^{1,2} However, PCM based on traditional phase-change materials like $\text{Ge}_2\text{Sb}_2\text{Te}_5$ (GST) suffers from high switching power and resistance drift, limiting its potential.¹

Here, using novel chalcogenide superlattices (SL) and leveraging their unique structural and electro-thermal properties, we realize ultralow-power PCM both on rigid and flexible substrates. Using SLs of alternating thin layers of Sb_2Te_3 and GeTe or GST, we achieved ~8-10x lower switching current density in superlattice-PCM on rigid silicon substrates, compared to conventional GST PCM.³ Our SLs are sputter-deposited at low temperatures (200 °C), compatible with CMOS back-end-of-line processing. Electro-thermal confinement in the superlattice material enhances the heating efficiency, enabling a dramatic reduction of switching energy in such PCM, as confirmed by our transport measurements and electro-thermal simulations.⁴

We also uncovered a key correlation between the SL interfaces and PCM device performance. We found that both switching current and resistance drift decrease as the SL period thickness is reduced, however, SL interface intermixing increases both.⁵ As the SL period thickness is reduced, a greater number of van der Waals (vdW) interfaces limits cross-plane thermal

¹ AVS Russell and Sigurd Varian Awardee

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transport, but if the SL interfaces are intermixed, the thermal conductivity can increase, due to the loss of vdW gaps.

We also integrated these superlattices directly onto flexible polyimide substrates in a confined memory cell, achieving further energy efficiency. Our flexible SL-PCM devices show record-low switching current density⁶ of 0.1 MA/cm², ~100x lower than commercial PCM. This memory also shows multi-level operation, promising for Internet-of-Things devices on flexible substrates.

In summary, we achieved ultralow-power switching in nanoscale phase-change memory based on chalcogenide superlattices. Our results demonstrate how combining versatile material functionalities and their transport fundamentals can unlock decade-spanning advances in energy-efficient memory for heterogeneously integrated nanoelectronics.

Refs: 1. S. Raoux *et al.*, *MRS Bull.* **39**, 703 (2014); 2. A. Sebastian *et al.*, *Nat. Nanotech.* **15**, 529 (2020); 3. A.I. Khan, E. Pop *et al.*, *IEEE EDL* **43**, 204 (2022); 4. H. Kwon, E. Pop *et al.*, *Nano Lett.* **21**, 5984 (2021); 5. A.I. Khan, E. Pop *et al.*, *Nano Lett.* **22**, 6285 (2022); 6. A.I. Khan, E. Pop *et al.*, *Science* **373**, 1243 (2021).

Electronic Materials and Photonics Division Room Oregon Ballroom 203-204 - Session EM-ThP

Electronic Materials and Photonics Poster Session

EM-ThP-1 Phase Transformation and Growth Mechanism of RF Sputtered Ferroelectric Lead Scandium Tantalate ($\text{PbSc}_{0.5}\text{Ta}_{0.5}\text{O}_3$) Films for Thermal Management, *Sanju Gupta*, Penn State University

Lead scandium tantalate ($\text{PbSc}_{0.5}\text{Ta}_{0.5}\text{O}_3$, PST), an order/disorder ferroelectric, is a potential candidate for electrocaloric cooling and pyroelectric IR detector. In this work, we report the phase transformation kinetics from two series of samples containing pure amorphous and mixture of amorphous and pyrochlore to desired perovskite phase using post-deposition rapid thermal processing (RTP) as well as growth mechanism of RF sputtered PST thin films using excess lead target on platinized silicon (Pt/Ti/SiO₂/Si) substrates. We find that small changes in the temperature ramp have a large effect on the degree of perovskite conversion (ferroelectric phase), orientation (crystallographic texture), and long-range order parameter ($\langle S_{111} \rangle$). Through isothermal annealing, we obtained optimal perovskite phase at $\geq 700^\circ\text{C}$ temperature. The phase transformation is characterized by spontaneous formation of center-type in-plane radial rosette-like structures revealed by scanning electron microscopy. The PST perovskite crystallites were found to coexist with pyrochlore in RTP annealed films. The volume fractions for perovskite and pyrochlore phase were obtained from the analysis of "rosettes" and respective x-ray diffraction intensities which helped to determine various parameters associated with phase kinetics (n , k , and activation energy, E_a) and accompanying growth. The effective activation energies of perovskite transition and growth were found to be 332 ± 11 kJ/mol (345 ± 11 kJ/mol) and 114 ± 10 kJ/mol (122 ± 10 kJ/mol), respectively, for pure amorphous only (and mixed amorphous and pyrochlore) phase following nucleation-growth controlled Avrami's equation. A linear growth rate ($n \sim 1$) for the perovskite phase indicates predominant interface-controlled process and diffusion-limited phenomena thus inhibiting rosette size owing to reactant depletion and soft impingement at the grain boundary. However, the growth behavior is isotropic in two-dimension parallel to the plane of the substrates for both sample series. Lead loss was severe for in-situ growth and RTP combined with conventional furnace annealing than those of RTP only films, which were closer to stoichiometric *albeit* with excess lead and marginal oxygen vacancies (V_o).¹

¹S. Gupta, J. Am. Cer. Soc. **106**, 2209-2224 (2023); <https://doi.org/10.1111/jace.18874>.

*Corresponding author: sgup77@gmail.com

EM-ThP-2 Flexible Phototransistors Array based on Hybrid Channel composed of Tellurium nanowires and tellurium-film with High Optical Responsivity, *Uisik Jeong*, Sungkyunkwan University (SKKU), Republic of Korea; *M. Naqi*, Sungkyunkwan University (SKKU), Pakistan; *S. Kim*, Sungkyunkwan University (SKKU), Republic of Korea

Tellurium (Te) has recently attracted substantial attention as a p-type channel material due to their favorable characteristics such as high transport properties, good photosensitivity, and piezoelectricity. Uniform and stable Te is important for the extensive applicability in terms of electronics and optoelectronics. Here, the novel hybrid channel of Te nanowires and Te-film for flexible p-type phototransistor arrays with highly linear photo-responsivity are reported for the first time. All the processes are conducted at a temperature lower than 100°C to reduce thermal budget on a flexible substrate. This paper includes optical properties of the TeNWs/Te-based FETs such as threshold voltage shift, photocurrent, responsivity, sensitivity, and time-domain behavior as well as electrical performance of those devices. The array consisting of 50 devices exhibits high mobility of $> 5 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ and $I_{\text{on}}/I_{\text{off}} > 10^4$ on average. More significantly, the stability of the devices is confirmed by the various tests such as positive/negative bias stress, illumination added bias stress, long-term stability response, and even mechanical bending stress, which exhibits stable and uniform characteristics of the devices.

EM-ThP-3 Observation of Gapless Nodal-line States in NdSbTe, *Sabin Regmi*, Idaho National Laboratory; University of Central Florida; *R. Smith*, A. Sakhya, M. Sprague, M. Mondal, I. Bin Elius, N. Valadez, University of Central Florida; *K. Gofryk*, Idaho National Laboratory; *A. Ptok*, D. Kaczorowski, Polish Academy of Sciences, Poland; *M. Neupane*, University of Central Florida

ZrSiS-type Lanthanide (*Ln*) based materials in the *LnSbTe* family bring the possibility of electronic correlations and magnetic ordering due to the presence of *Ln 4f* electrons in addition to the topology that the ZrSiS-type systems are well known for. Here, we carried out an angle-resolved photoemission spectroscopy (ARPES) study of Neodymium-based NdSbTe, supported by first-principles calculations and thermodynamic measurements. Thermodynamic measurements reveal a magnetic transition into an antiferromagnetic ground state at around 2 K. The paramagnetic phase ARPES results detect the presence of multiple gapless nodal lines, which is also supported by first-principles calculations. Two of such nodal lines reside along the bulk X-R high-symmetry direction and one lies across the Γ -M direction forming a diamond plane centered at the Γ point. Overall, this study reveals the topological electronic structure of NdSbTe and presents a new platform to understand how such electronic structure evolves with spin-orbit coupling tuning across the *LnSbTe* family.

*This work is supported by the National Science Foundation under CAREER Award No. DMR-1847962 and the Air Force Office of Scientific Research MURI Grant No. FA9550-20-1-0322.

EM-ThP-4 Growth of Mn-Doped $\text{Pb}(\text{In}_{1/2}\text{Nb}_{1/2}\text{O}_3)$ - $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3}\text{O}_3)$ - PbTiO_3 Thin Films by Pulsed Laser Deposition, *Da-Ren Liu*, Taiwan Instrument Research Institute, National Applied Research Laboratories, Taiwan

Because of their extraordinary large electromechanical coupling coefficient and piezoelectric coefficient, relaxor-based ferroelectric crystals $\text{Pb}(\text{In}_{1/2}\text{Nb}_{1/2}\text{O}_3)$ - $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3}\text{O}_3)$ - PbTiO_3 (PIN-PMN-PT) and Mn-Doped $\text{Pb}(\text{In}_{1/2}\text{Nb}_{1/2}\text{O}_3)$ - $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3}\text{O}_3)$ - PbTiO_3 (Mn:PIN-PMN-PT) with morphotropic phase boundary (MPB) have attracted extensive attention. The PIN-PMN-PT and Mn:PIN-PMN-PT not only have similar piezoelectric performance to that of the binary PMN-PT but also possesses higher phase transition temperature and coercive field. They also become important materials in the fabrication of high-performance electromechanical devices including transducers, actuators and sensors. In this study, highly textured thin films of the Mn:PIN-PMN-PT were grown on SrTiO₃ substrates by Nd:YAG pulsed laser deposition (PLD). According to the results of glancing-angle x-ray powder diffraction (GAXRD), the Mn:PIN-PMN-PT films are polycrystalline. The thickness and roughness of the films were characterized by grazing-incidence x-ray reflectivity (GIXR), and the piezoelectric constant d_{33} was measured by the piezoelectric force microscopy (PFM). The complex refractive indices were measured in the range from 1.5 to 4.0 eV by spectroscopic ellipsometry (SE). The average oscillator strength and its associated wavelength were estimated by using a Sellmeier-type dispersion equation.

EM-ThP-5 Synthesis and Stability of MBE Grown NbSe₂, *C. Rogers*, University of Virginia; *A. Hasan*, The University of Virginia; *C. Jezewski*, *C. Naylor*, Components Research, Intel Corporation, Hillsboro, OR 97124, USA; *N. Shukla*, *Stephen McDonnell*, The University of Virginia

Metallic 2D materials offer a unique pathway to aggressive thickness scaling without sacrificing resistivity. Unlike conventional metals which see significant increases in resistivity, when the thickness is on the order of the electron mean free path, due to increase surface/interface scattering, for 2D materials the conduction is already largely confined to the individual layers with negligible transport across the van der Waals gaps. As such, when scaled into the nm regime, these materials see little or no increase in their resistivity.

Niobium diselenide (NbSe₂) is a metal-like transition metal dichalcogenide that has a similar crystal structure to the well-studied 2H-MoS₂. In our work, NbSe₂ is grown by molecular beam epitaxy and is shown to naturally deposit with self-intercalated Nb in the van der Waals gap. We demonstrate how the resistivity of NbSe₂ varies as a function of deposition temperature and flux ratio and then turn our focus to how the oxidation behavior of the thin films. Specifically, we show that the grown temperature of the thin films impacts their subsequent stability in air, likely due to differing grain sizes. In addition to this we show that some processing steps that are typically nanoelectronic device fabrication can also oxidize the material which suggests that due consideration must be taken if this material is to be integrated into any device architectures.

Thursday Evening, November 9, 2023

EM-ThP-6 Hollow-Cathode Plasma-ALD of Titanium Nitride Films Using *In-Situ* Ellipsometry for Conductivity Analysis, D. Lefcort, S. Bin Hafiz, H. Mohammad, L. Antoine, N. Ibrahimli, S. Ilhom, University of Connecticut; A. Okyay, OkyayTech Inc; **Necmi Biyikli**, University of Connecticut

Conducting TiN films are used in various CMOS device layers. As the trend towards highly complex and 3D device architectures continue along with continued scaling in the deep single-digit nanometer level, low-temperature and conformal deposition of precision thickness controlled TiN films are critically needed. Based on our achievements in crystalline III-nitride films using hollow-cathode plasma-assisted atomic layer deposition (HCP-ALD), in this study we have investigated TiN film deposition at 200 °C using the very same reactor. We have used *in-situ* ellipsometry to analyze the evolution of film resistivity using various fitting models including Drude-Lorentz and Drude dispersion models. We share our experimental findings on how the TiN film properties were impacted by the HCP-ALD process conditions as well as how the *in-situ* extracted film resistivity values compare with ex-situ measured resistivities.

The TiN films were deposited using metal-alkyl titanium precursor (tetrakis(dimethylamido)titanium) – TDMAT and various nitrogen/hydrogen plasma mixtures (N₂/H₂ at various flow rates) at 200 °C substrate temperature and 50 – 100 W RF-power range. SiO₂-coated Si(100) wafer and glass slide samples were utilized as substrates for TiN film deposition. Real-time *in-situ* ellipsometry data was recorded using a multiwavelength ellipsometer unit. TiN films grown at lower power values (50 vs 100 W) exhibited lower film resistivity values. The total N₂/H₂ plasma gas flow and chamber pressure showed a significant impact on the film conductivity: When compared to 100/100 sccm plasma flow, 20/20 sccm samples grown on SiO₂/Si(100) substrates displayed the lowest resistivity values reaching ~150 micro-ohm.cm. Grazing-incidence XRD (GIXRD) measurements revealed polycrystalline TiN films on SiO₂/Si(100) substrates. The Drude-Lorentz and Drude dispersion model layer fitting results compare reasonably well with the Van der Pauw sample measurements, verifying the effectiveness of *in-situ* ellipsometry for real-time film conductivity analysis.

EM-ThP-7 A Statistical Design of Experiments and Structural Characterization of ITO for Perovskite Solar Cells, **Firdos Ali**, Metallurgical and Materials Engineering, The University of Alabama; **D. Li**, Electrical and Computer Engineering, The University of Alabama; **S. Gupta**, Metallurgical and Materials Engineering, The University of Alabama

We have optimized the processing and annealing of sputtered indium-tin oxide (ITO) thin films for solar cell applications by DC magnetron sputtering. The effects of process parameters such as deposition power, reactive gas flow percentage, annealing temperature and time, as well as film thickness, on the sheet resistance and transmission of the ITO films was systematically studied, using a Design of Experiments. Additionally, structural characterization of the deposited films was performed using various techniques, including X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), four-point probe, UV-VIS spectrometry, and atomic force microscopy (AFM). TEM analysis revealed grain boundaries, crystallinity, and d-spacing of ITO thin film. The grain size was calculated with the help of the Scherrer equation. The XRD spectra of the ITO films revealed a polycrystalline structure with preferred (222) orientation of the ITO film. The SEM image of the ITO target gives information about the morphology of the racetrack after sputtering. The topography and surface roughness were evaluated by atomic force microscopy (AFM). A sheet resistance of 10 ohms/sq. and transmission of over 90% over 400-700 nm wavelengths was achieved. Perovskite solar cells fabricated with these optimized ITO electrodes showed promising properties.

EM-ThP-8 Voltage Tunability in Foundry Produced Resonant PZT piezoMEMS, **J. Evans**, **N. Montross**, **Sean Smith**, **S. Chapman**, **M. McDaniel**, Radiant Technologies Inc.

Radiant Technologies recently launched our Thin Film Foundry capable of producing a wide variety of structures. Radiant has been fabricating PZT thin films since 1990 while performing foundry services on a word-of-mouth basis. Over time our process has increased in capability and can now create released MEMS. We have also formalized our design rules and are now offering foundry services to the broader community.

As a part of our process development, we demonstrated a variety of structures such as membranes and beams fixed at one or two ends, with and without tip masses. Released structures can have resonant modes ranging from 100s of Hz to 10s of kHz. These can be plugged into customer's projects or serve as a starting point for a custom design. We collaborate with customers to integrate our PZT capacitors into another stack/process or to deposit their unique sensor material/structure onto a piezoMEMS device.

In this presentation the voltage tunability of our released piezoMEMS structures will be demonstrated along with a brief overview of our foundry process and some examples of what our customers have been able to produce with it.

EM-ThP-9 Enforcing π - π Stacking Using a 1D Perovskite Core, **Raúl Castañeda**, New Mexico Highlands University

During the past decade, hybrid organic-inorganic metal halides have attracted the attention of a broad group of institutions due to the many potential applications these materials can have, such as semiconductors, solar cells, and LEDs. More specifically, manganese-halide compounds have been studied for their emission properties and potential applications in X-ray detectors. In this work, four new manganese(II) chloride and manganese(II) bromide 1D coordination polymers were synthesized with 4-ethylpyridine (4-ETP) or 4-phenylpyridine (4PhP) and characterized by single-crystal X-ray diffraction. These materials have a manganese core surrounded by four edge-sharing halide atoms (MnX₄) and the ligand coordinating from above and below the MnX₄ plane. Interestingly π - π interactions are enforced by the 1D coordination polymer. Further studies on these types of materials can result in new molecular wires as semiconductor materials.

EM-ThP-10 Modular until it's Not – Imaging Fast, Hard X-Rays at NIF, **Mary Ann Mort**, University of California at Davis; **A. Carpenter**, Lawrence Livermore National Lab; **C. Hunt**, University of California at Davis

The proposed multi-frame gated x-ray imager (MGXI) is a fast, hard x-ray imaging diagnostic for use in ICF and HED experiments at the National Ignition Facility (NIF), such as Compton radiography and hot spot imaging. MGXI has goals to image 10-100 keV x-rays with 100-1000 ps temporal resolution in 2-8 frames and >5% DQE. Modularity of the versatile testbed for initial MGXI component experimentation starts with testing microchannel plates (MCPs) under vacuum with an electron gun and a simple photodiode (PD) array. Simultaneously, MCPs will be modeled in Computer Simulation Technology (CST) to determine the effects an applied magnetic field has on the electron trajectories.

Friday Morning, November 10, 2023

2D Materials Technical Group

Room C123 - Session 2D+EM-FrM

2D-Materials: Device Application

Moderators: Maria Hulse, Pennsylvania State University, **Tongcang Li**, Purdue University

8:20am 2D+EM-FrM-1 Stochastic Computing Enabled by 2D Memtransistors, **Saptarshi Das**, Pennsylvania State University **INVITED**

In the emerging era of artificial intelligence, deep learning, and Big-data, the energy and hardware investments required for conventional high-precision digital computing are becoming increasingly unsustainable. As a result, there is a growing need for a new paradigm that prioritizes energy and resource efficiency over precision for many computing applications. Stochastic computing (SC) is a promising alternative because it can perform basic arithmetic operations using simple logic gates, unlike digital computers that require many logic gates and a high transistor volume. However, the hardware investment necessary to generate stochastic bits (s-bit), the fundamental computing primitive for SC, has hindered its widespread adoption. While traditional silicon complementary metal oxide semiconductor (CMOS) technology can accelerate SC, it still requires extensive hardware investment. Memristor and spin-based devices offer natural randomness but rely on hybrid designs involving CMOS peripherals, which increase the area and energy burden.

To overcome these limitations, we have developed a standalone SC architecture embedded in memory based on two-dimensional (2D) memtransistors. This monolithic and non-von Neumann SC architecture requires only a tiny amount of energy (< 1 nano Joules) for s-bit generation and to perform arithmetic operations, and occupies a small hardware footprint, highlighting the benefits of SC. Additionally, the researchers demonstrate the acceleration of Bayesian inference using their SC platform.

9:00am 2D+EM-FrM-3 Electrical Characteristics of Semi-Metallic 2H-NbSe₂ for Scalable Interconnects, **Abir Hasan**, *T. Alem, C. Rogers, S. Stevenson, S. McDonnell, N. Shukla*, University of Virginia

Despite Copper being the current material of choice for interconnect technology, it suffers from increased resistivity at scaled dimensions and the necessity for a barrier-liner to prevent diffusion. This has motivated the exploration of alternate materials that can overcome these limitations for scaled CMOS technology nodes. Metallic 2D materials can offer a promising option. In this work, we evaluate the properties of 2D semi-metallic material 2H Niobium diselenide (2H-NbSe₂) as a candidate for realizing highly scalable interconnect technology without the need for barrier-liner. We performed detailed electrical characterization evaluating the dimensional scaling, dependence of the resistivity on temperature, device lifetime, effect of encapsulation layer etc. on ribbon devices fabricated with 2H-NbSe₂ material. 2H-NbSe₂ showed negligible change in resistivity compared to the bulk value when scaled down to thicknesses less than 15 nm. High current density transport measurements are performed on 2H-NbSe₂ ribbon devices with varied width (0.1-1um) at elevated temperature (>= 100°C) to assess the reliability and failure characteristics. Lifetime of the NbSe₂ ribbons improved when an Al₂O₃ encapsulation layer was used. Our work provides critical insights into the potential of NbSe₂ for realizing scalable interconnects.

9:20am 2D+EM-FrM-4 Magneto-Transport Measurement and Maximum Entropy Mobility Spectrum Analysis in Semiconductor Substrates for Graphene Growth, **Ruhin Chowdhury**, University of New Mexico; *A. Majeed, Intel Corp.; E. Renteria, D. Ghosal*, University of New Mexico; *M. Arnold, M. Lagally*, University of Wisconsin - Madison; *F. Cavallo*, University of New Mexico

Our study focuses on the multi-carrier electrical transport characterization of heat-treated bulk Ge near its melting point. Single-crystalline Ge has recently gained relevance as a substrate for the chemical vapor deposition (CVD) of high-quality graphene sheets, nanowires, and nanoscale wigglers.^{1,2} Deposition of graphene on (110) Ge substrates allows integration of a 2D sheet with widely used semiconductors without the need for release and transfer processes, which may lead to the degradation of graphene's structural and functional properties. Determining the full potential of graphene/Ge for electronic applications requires understanding charge transport in this material combination. To date, quantitative models of lateral charge transport in graphene/Ge (i.e., transport of mobile carriers in the direction parallel to the graphene/Ge interface) are not available, primarily due to the overwhelming contribution of bulk Ge. In this work, we

isolated and identified all mobile carrier types undergoing drift in heat-treated Ge at the typical condition for CVD of monolayer graphene. We believe these results to be the basis for quantifying carrier mobilities, carrier concentrations, and carrier types in graphene/Ge.

We performed magneto-transport measurements of heat-treated Ge between 50 K and 400 K and a magnetic field spanning from -7T to 7T to extract the conductivity tensor of the material. The Ge substrates were nominally intrinsic before annealing. Next, we used maximum entropy mobility spectrum analysis (MEMSA)³ to identify the carrier types contributing to transport in Ge (110). Our analysis consistently shows the contribution of heavy holes (HH) and light holes (LH) in bulk Ge. The excess holes in bulk Ge are attributed to the formation of acceptor-like vacancies during high-temperature annealing of Ge.⁴ The trend of carrier mobility vs. temperature indicates that different scattering mechanisms are dominant for HH and LH in a given temperature range. In addition to the contribution of HH and LH in bulk Ge, we identified two additional carrier types, namely electron and ultra-low mobility holes. We attribute the electrons to donor-type interstitials and the low-mobility holes to accumulated HH near the native oxide/Ge interface.

ACKNOWLEDGMENT. This work was supported by the U.S. AFOSR and Clarkson Aerospace Corporation under award No. FA9550-21-1-0460/UNM 21-1-0460.

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9:40am 2D+EM-FrM-5 What Are 2D Materials Good for?, **E. Pop, Tara Pena**, Stanford University **INVITED**

This talk will present my (biased!) perspective of what two-dimensional (2D) materials could be good for. For example, they could be good for applications where their ultrathin nature gives them distinct advantages, such as flexible electronics [1] or light-weight solar cells [2]. They may not be good where conventional materials work sufficiently well, like transistors thicker than a few nanometers. I will focus on 2D materials for 3D heterogeneous integration of electronics, which presents major advantages for energy-efficient computing [3]. Here, 2D materials could be monolayer transistors with ultralow leakage [4] (due to larger band gaps than silicon), used to access high-density memory [5]. Recent results from our group [6,7] and others [8] have shown monolayer transistors with good performance, which cannot be achieved with sub-nanometer thin conventional semiconductors, and the 2D performance could be further boosted by strain [9]. I will also describe some unconventional applications, using 2D materials as thermal insulators [10], heat spreaders [11], and thermal transistors [12]. These could enable control of heat in “thermal circuits” analogous with electrical circuits. Combined, these studies reveal fundamental limits and some unusual applications of 2D materials, which take advantage of their unique properties.

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10:40am **2D+EM-FrM-8 Effect of Temperature on the Surface Morphologies of Sulfurized-Grown WS₂**, *Md Samim Reza, M. Singh*, Indian Institute of Technology Delhi, India

Tailored morphologies are essential for realizing the diverse applications of tungsten disulfide. This work reports on a successful growth of WS₂ that involves the sulfurization of a sputter-deposited (Angstrom Engineering Evovac) thin film of tungsten (150-300 Å with a rate of 0.4 Å/s) on a SiO₂ substrate (University Wafers) and the effect of temperature on the surface morphology of as-grown WS₂. The as-deposited tungsten substrate was cut into 2cm x 2cm and placed inside a custom-design horizontal CVD system (Quazar Technologies). A sulfur (99.5% pure precipitated powder, 600-1000 mg, Sigma Aldrich) was placed upstream (20-40 cm) from the tungsten heating zone (700-1000 °C) to grow WS₂ under a carrier gas (Ar) flow of 0-400 sccm. Raman spectroscopy (514 nm laser source with a spot size of ~1 μm² for 100x objective, 1mW power, Renishaw inVia) revealed the peaks at ~350/cm and ~417/cm, confirmed the growth of WS₂ and the peak intensity ratio of in-plane and out-of-plane ($E_{2g}^1/A_{1g}^1 < 1$), suggest a multilayer growth [1]. The X-ray diffraction (Rigaku Ultima IV) analysis indicates the growth of hexagonal-phased WS₂ (JCPDS: 08-0237) with a mixed plane to a (002)-dominated at higher temperatures. The field emission scanning electron microscopy (Magna LMU, Tescan) scans revealed the growth morphology from a planar to a nanoflower, forming a thin film of WS₂. Different sulfurization temperatures result in distinct morphologies, with a thin film morphology obtained at 700-750°C, followed by the dominance of nanoflower-like WS₂ structures between 850°C and 950°C as observed by field emission scanning electron microscopy. At temperatures higher than 950°C, WS₂ nanoflowers with vertical alignment are grown on a SiO₂ substrate. Electron dispersive X-ray (EDX, Ametek) spectra show a stoichiometry close to 1:2 for W: S. The atomic force microscope analysis (Dimension Icon, Bruker) revealed that surface roughness (sputter-deposited tungsten roughness of ~80 pm) increased from ~5 to 80 nm with the growth temperature. The experimental results emphasize the importance of temperature in determining the surface morphologies of WS₂. The ability to control the growth temperature offers customization of WS₂ morphologies that could allow the fabrication of WS₂-based devices with the desired properties [2-3].

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11:00am **2D+EM-FrM-9 The Study of Internal Ion Transport in Ionic CuiP₂S₆**, *Yujie Sun, B. Liu*, Tsinghua University, China

Memristor-based neuromorphic computing is promising for artificial intelligence. However, most of the reported memristors have limited linear computing states and consume large operation energy which hinder their applications. Herein, we report a memristor based on ionic two-dimensional CuiP₂S₆ (2D CIPS), in which up to 1350 linear conductance states are achieved by controlling the migration of internal Cu ions in CIPS. In addition, the device shows a low operation current of ~100 pA. Cu ions are proven to move along the electric field by *in-situ* scanning electron microscopy and energy dispersive spectroscopy measurements. Furthermore, complex signal transport among multiple neurons in the brain is imitated by 2D CIPS-based memristor arrays. Our results offer a new platform to fabricate high-performance memristors based on ion transport in 2D materials for neuromorphic computing.

Applied Surface Science Division

Room B117-119

Session

AS+2D+CA+EM+MS+NS+SE+SS+TF-FrM

Industrial Applications

Moderators: Marko Sturm, University of Twente, Netherlands, Alan Spool, Western Digital Corporation, Yundong Zhou, National Physical Laboratory, UK

8:20am **AS+2D+CA+EM+MS+NS+SE+SS+TF-FrM-1 Correlative Analysis Using Time-of-flight Secondary Ion Mass Spectrometry for Beam Sensitive Samples**, *Jean-Paul Barnes, C. Guyot, P. Hirschhahn, A. De Carvalho, N. Gauthier, T. Maindrion, B. Gilquin, D. Ratel, C. Gaude, O. Renault*, Univ. Grenoble Alpes, CEA, Leti, France; *A. Galtayries*, Chimie ParisTech, PSL University, CNRS, Institut de Recherche de Chimie Paris, France; *G. Fisher*, Physical Electronics USA; *C. Seydoux, P. Joanneau*, Univ. Grenoble Alpes, CEA, IRIG-MEM, France

INVITED

Time-of-flight Secondary Ion Mass Spectrometry (TOF-SIMS) is now widely used for materials analysis in domains such as semiconductor and energy applications. These challenging applications also provide access to well-controlled, custom made samples that have allowed the limits of TOF-SIMS analysis to be identified and helped in the development of correlative analysis approaches. Recent examples include combining AFM measurements with TOF-SIMS depth profiling to correct for sputter rate differences [1] or to measure mechanical or electrical properties and performing X-ray tomography prior to FIB-TOF-SIMS analysis to allow morphological and compositional data from the same volume to be visualized [2]. Currently we are working on two aspects. Firstly improving the quantification and chemical sensitivity of the technique by combining TOF-SIMS with photoemission techniques (XPS or XPEEM), and secondly trying to improve the lateral resolution by correlation with SEM and AFM measurements. Recent examples will be shown for the analysis of beam sensitive organic samples such as OLED devices, brain tissue samples after medical device implantation [3] and symbiotic microorganisms [4]. As well as the correlative aspects between techniques, we will show how tandem mass spectrometry can help in analyzing complex organic samples. In all cases the importance of sample preparation is paramount, especially for biological samples. For example, for the correlation between TOF-SIMS and XPS on OLED samples, a wedge crater protocol has been developed to allow analysis on exactly the same area of the sample whilst minimizing beam damage to the sample. Wedge crater preparation and transfer between instruments is performed under a protected environment (vacuum or inert gas) to avoid unwanted surface modifications.

Part of this work, carried out on the Platform for Nanocharacterisation (PFNC), was supported by the "Recherches Technologiques de Base" and the "CARNOT" program of the French National Research Agency (ANR).

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9:00am **AS+2D+CA+EM+MS+NS+SE+SS+TF-FrM-3 Secondary Ion Mass Spectroscopy of Battery Surface and Interface Chemistry – Metrology and Applications**, *Yundong Zhou, S. Marchesini, X. Yao, Y. Zhao, I. Gilmore*, National Physical Laboratory, UK

Batteries are very important to achieve carbon net zero. Understanding battery materials change, electrode surfaces, solid electrolyte interphase (SEI) evolution and novel solid-state electrolyte structures is very helpful for developing better batteries. Surface chemical analysis techniques such as X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy are often used but they have their limitations. XPS analysis cannot always resolve overlapping binding energies for some key SEI elements. The SEI often has poor Raman signal intensity. These are all hurdles for battery applications.

Secondary ion mass spectrometry has great potential to study interfacial chemistry in batteries owing to high sensitivity and high-resolution imaging in 2D and 3D. In this study, we use an OrbiSIMS instrument which is equipped with two complementary mass spectrometers (MS). A time-of-flight (ToF) MS has the capability for 2D and 3D imaging using a Bi³⁺ liquid metal ion gun with a spatial resolution of up to 200 nm but with modest mass resolving power. The Orbitrap MS offers high mass resolution and mass accuracy (> 240,000 at m/z 200 and < 2 ppm, respectively). The instrument is equipped with low energy Cs and O₂ sputter beams for high resolution depth profiling of inorganic materials. It also has a Leica docking station enabling samples to be transferred using a vacuum sample transfer

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chamber from an argon glove box without atmospheric exposure. To improve the quality of measurements on battery materials, we have used ion implanted materials to determine relative sensitivity factors for relevant elements. We have also conducted a systematic study to optimise the OrbiSIMS depth profiling capability. These findings along with recommendations to reduce effects of signal saturation will be discussed and examples of the application to batteries will be provided. We will provide examples of the application of ToF MS and Orbitrap MS. (1,2)

1. X. Yao et al., Energy Environ. Sci., 2023, DOI: 10.1039/D2EE04006A.
2. S. Marchesini et al., ACS Appl. Mater. Interfaces, 14(2022)52779-52793.

9:20am **AS+2D+CA+EM+MS+NS+SE+SS+TF-FrM-4 Characterizing Ion Distribution at the Solid-Electrolyte Interface in Solid-State Lithium Ion Batteries with ToF-SIMS, Teodora Zagorac**, University of Illinois - Chicago; M. Counihan, J. Lee, Y. Zhang, Argonne National Laboratory, USA; L. Hanley, University of Illinois - Chicago; S. Tepavcevic, Argonne National Laboratory, USA

Interest in solid state lithium-ion batteries as the next generation of energy storage devices has led to intense study of the chemistry, structure, and manufacturing processes for polymer electrolytes. Lithium bis(trifluoromethanesulfonyl) imide (LiTFSI) salt is often used to introduce Li ions into the solid-state electrolyte. Lithium bis(fluorosulfonyl)imide salt (LiFSI) and lithium nitrate (LiNO₃) are less expensive salts with the potential to improve performance characteristics over pure LiTFSI in certain electrolyte formulations. The differences in distribution and reactivity of these different salts are still unknown but are critical to battery performance. Time-of-flight secondary ion mass spectrometry (ToF-SIMS) imaging and depth profiling was performed to compare the distributions of Li⁺ cations and TFSI⁻, FSI⁻, and NO₃⁻ anions across the solid-electrolyte interface (SEI) formed between the polymer electrolyte and thin lithium metal electrode. Experiments were performed on ~600 nm salt-rich poly(ethylene oxide) electrolytes with ~10 nm overlayers of vapor-deposited Li metal. Samples were probed with 30 keV Bi₃⁺ from a liquid metal ion gun while depth profiling with 10 keV Ar₁₄₀₀ gas cluster ion beam to collect both positive and negative ion mass spectra. Ion distributions from the three salts and their 3D images will be presented and discussed in terms of the relative composition of their SEI layers. Chemical differences from ToF-SIMS analysis help explain the differences in electrochemical SEI formation and half cell cycling: LiTFSI and LiFSI are similar, but LiNO₃ presents much different electrochemical properties.

9:40am **AS+2D+CA+EM+MS+NS+SE+SS+TF-FrM-5 A Perspective on X-ray Photoelectron Spectroscopy (XPS) Peak Fitting, and Reporting of XPS Data Acquisition and Peak Fitting Parameters in the Literature, Matthew Linford**, G. Major, J. Pinder, Brigham Young University

We recently reported that a rather large fraction (ca. 40 %) of the XPS peak fitting in the literature is at best suspect. In a recent Perspective article (doi: 10.1116/6.0002437) we argue that the various stakeholders of the problem can act together to improve the current situation. This Perspective begins with representative examples of poor XPS peak fitting. The purpose of showing these examples is to demonstrate to the reader that we are not quibbling or arguing over subtle interpretations of the data. Increasingly, we see errors that might be classified as egregious. We argue that science is in a state of 'pre-crisis' more than in a state of 'crisis'. We suggest that if too much incorrect data analysis enters the literature it may cease to be self-correcting. We note the very large number of surface and material characterization techniques available today and how this presents a challenge for scientists. Consequently, it is likely that many manuscripts are incompletely reviewed today. Graduate students and post-docs at research institutions are often given minimal training on acquiring and analyzing XPS data. High fees for instruments can limit access to them and student training. Prisoner's dilemmas may help explain situations in science that lead to suboptimal outcomes for the community. Authors are primarily responsible for the quality of the research in their papers, not reviewers or editors. We question the wisdom of placing the names of reviewers and editors on papers. In some cases, staff scientists are not adequately recognized for their intellectual contributions to projects. Selective reviewing may allow more reviews to be performed without overtaxing the community. Reviewing at some open access journals may be inadequate. Collaboration needs to be encouraged to a greater extent at some institutions.

10:00am **AS+2D+CA+EM+MS+NS+SE+SS+TF-FrM-6 Unsupervised and Supervised Machine Learning Applied to ToF-SIMS of an Organic Matter-Rich Mudstone with Molecular Biomarker**, M. Pasterski, University of Illinois Chicago; M. Lorenz, Oak Ridge National Laboratory; A. Ievlev, Oak Ridge National Laboratory; R. Wickramasinghe, Luke Hanley, F. Kenig, University of Illinois Chicago

Time-of-flight secondary ion mass spectrometry (ToF-SIMS) imaging has been used to detect organic compounds including molecular biosignatures (biomarkers) in geologic samples (R.C. Wickramasinghe, *et al.*, Anal. Chem., 2021, 93, 15949). The spatial distribution of these biomarkers can help determine when and how these organics were incorporated into the host rock. ToF-SIMS imaging can rapidly collect a large amount of data, but molecular and fragment ions of different species are mixed together in complex mass spectra that are difficult to interpret. Here, we apply unsupervised and supervised machine learning (ML) to help interpret the mass spectra obtained by ToF-SIMS of an organic-carbon-rich mudstone from the Middle Jurassic of England (UK). It was previously shown that the presence of sterane molecular biomarkers in this sample can be detected via ToF-SIMS (M.J. Pasterski, *et al.*, Astrobiol., in press). We use unsupervised ML on field emission scanning electron microscopy – electron dispersive spectroscopy (SEM-EDS) measurements to define compositional categories based on differences in elemental abundances. We then test the ability of four ML algorithms - k-nearest neighbors (KNN), recursive partitioning and regressive trees (RPART), eXtreme gradient boost (XGBoost), and random forest (RF) - to classify the ToF-SIMS spectra using the categories assigned via SEM-EDS, using organic and inorganic labels, as well as using presence or absence of detectable steranes. KNN provided the highest predictive accuracy and balanced accuracy. The feature importance, or the specific features of the ToF-SIMS data used by the KNN model to make classifications could not be determined, preventing post-hoc model interpretation. However, the feature importance extracted from the other three models was useful for interpreting spectra. We determined that some of the organic ions used to classify biomarker containing spectra may be fragment ions derived from kerogen.

10:40am **AS+2D+CA+EM+MS+NS+SE+SS+TF-FrM-8 Probing Thin Film Interfaces at the Nanoscale by Low Energy Ion Scattering**, Marko Sturm, A. Chandrasekaran, A. Valpreda, A. Zameshin, R. Van de Kruijs, A. Yakshin, F. Bijkerk, M. Ackermann, University of Twente, Netherlands **INVITED**

The growth of thin films with nanometer range thickness is of great importance for application topics as nanoelectronics, oxidation protection of thin films and optical coatings for X-ray applications. The performance of these coatings often critically depends on the sharpness of the interfaces between different layers. In this talk I will outline how we use Low-energy ion scattering (LEIS) to study interface formation between layers of different transition metals (TMs) and between TMs and Si.

LEIS with noble gas ions as projectiles yields surface peaks that indicate the composition of the outermost atomic layer of a sample. This makes the technique excellently suited to study whether deposition of a thin film leads to a closed layer. However, deposition of an overlayer on top of an underlayer may result in surface segregation of underlayer atoms (driven by surface energy differences or stress), such that the surface composition is not directly representative for the in-depth concentration profile. We analyzed the evolution of surface coverage versus deposited thickness for a large set of TM/TM film combinations, deposited by magnetron sputtering in a system that allows LEIS analysis without vacuum break after deposition. By applying a model that takes into account surface segregation, the interface profiles were derived from these layer growth profiles, which we call deposition depth profile. In addition, we demonstrated that the sharpness of interfaces in TM/TM film systems can be predicted by a phenomenological model with the crystal structure and surface energy of the materials as input parameter. This model in principle predicts the sharpness of the interface in any TM/TM thin film combination! [1]

Apart from surface peaks, LEIS spectra typically also contain so-called tails, caused by projectiles that, after sub-surface scattering, are reionized when leaving the sample. It was demonstrated before that LEIS tails can be used to determine thickness of various thin film systems, when the stopping power of the projectiles is known. Here, we show that LEIS tails can also be used to determine the sharpness of interfaces of few nm Si-on-W and Si-on-Mo films, by comparing LEIS measurements with Monte Carlo simulations with the TRBS code, which takes into account multiple scattering and stopping in the target. This approach allows interface characterization from a single sample, without the need to make a deposition depth profile.

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References:

[1] A. Chandrasekaran, R.W.E. van de Kruijs, J.M. Sturm, A.A. Zameshin and F. Bijkerk, ACS Applied Materials & Interfaces **11**, 46311 (2019)

11:20am AS+2D+CA+EM+MS+NS+SE+SS+TF-FrM-10 The Effect of Instrument Settings, Sample Distance, and Tilt on TofsimSecondary Ion Intensities, *Alan Spool, L. Finney*, Western Digital

Experiments were performed to explore the effects of various instrument settings and sample placements on secondary ion intensities to better understand what factors have the greatest effect on repeatability and replicability in TOF-SIMS. A batch of magnetic recording disks used in hard disk drive manufacture, natively flat and homogeneous, were used as test samples for the purpose. As expected, by far the largest variable altering raw intensities was the LMIG tip stability. LMIG tips can have stable emission currents while still producing variable pulsed LMIG beam currents with resultant variable secondary ion counts. This variability sometimes is seen in slow current drift, but is sometimes so rapid that measurements taken directly before each measurement are not close enough in time to properly scale the measurement results. In these cases, normalization is the only solution. Secondary ion intensities were remarkably insensitive to small variations in sample height (position relative to the extractor). Far more interesting were the changes to the secondary ion intensities that resulted from tilting the sample. These effects varied amongst the secondary ions detected such that normalization did not remove them. Secondary ion emission as a function of emission angle has long been understood to be like a cosine function and to vary somewhat from ion to ion. These different angular profiles explain the differences seen in ion detection as a function of tilt. Some of these differences proved to be asymmetrical, varying depending on whether the sample was tilted toward or away from the primary ion source, an indication that in some situations some residual momentum from the initial primary ion impact onto the surface is carried into the secondary ion emission. These results have implications for attempts to do quantitative analysis on any sample that is not completely flat.

11:40am AS+2D+CA+EM+MS+NS+SE+SS+TF-FrM-11 Evaluation of Unaltered and Irradiated Nuclear Graphite Surfaces through Integrated Traditional XPS and HAXPES Techniques, *Jonathan Counsell, L. Soomary, K. Zahra*, Kratos Analytical Limited, UK; *B. Spencer, A. Theodosiou*, University of Manchester, UK

Graphite-moderated reactors have been operational worldwide for several decades. There exists a substantial body of research in this domain, with particular emphasis on investigating the impact of irradiation damage on the graphite matrix. In order to satisfy the design and regulatory requisites of these advanced reactors, it becomes imperative to gain a deeper comprehension of the retention and transportation mechanisms of fission products within graphite.

This study outlines a technique for the precise assessment of the surface chemistry of highly-oriented pyrolytic graphite (HOPG), serving as a representative model akin to the current graphite grades utilized in the nuclear sector. We delve into the process of surface etching aimed at eliminating surface adsorbates and contaminants. This process involves the utilization of both monatomic and cluster ions, the former inadvertently causing undesirable damage to the graphite structure. Such damage is evidenced by a significant reduction in the sp² component of C 1s. We introduce the use of UPS analysis as a straightforward means of determining the presence of sp² characteristics in the uppermost atomic layers.

Moreover, we examine the consequences of high-energy ion implantation (Cs⁺) and the ensuing damage to the HOPG surface. This examination is carried out using XPS (1486eV) and HAXPES (2984eV), thereby showcasing the capability to characterize the resulting surface damage and the associated alterations within the probed depths.

Electronic Materials and Photonics Division

Room B116 - Session EM1+TF-FrM

Advanced Patterning and Fabrication for Device Scaling

Moderators: **Stephen McDonnell**, University of Virginia, **Michelle Paquette**, University of Missouri-Kansas City

8:20am EM1+TF-FrM-1 Thin Film Challenges and Opportunities in a 3D-Evolving Memory Landscape, *Johan Swerts*, imec, Belgium **INVITED**

Device architectures used in SRAM memory transitioned in the past decade from the historical 2D planar transistor to FINFET. The next innovation revealed for the 3nm node is a 3D stacked gate-all-around architecture in combination with a backside power delivery network. For further scaling, stacking nmos and pmos, the so-called complementary-FET (CFET) design, is envisaged to happen in 2030. New metallization schemes to tackle the RC challenge as device dimensions of the interconnects shrink, such as Cu replacements materials in a direct metal etch integration scheme. A broad variety of complementary deposition techniques and introduction of new materials will be needed to enable the above-mentioned novelties.

A similar trend towards stacking functional cells can be observed in various memories, such as the emerging memories that aim to bridge the gap between DRAM and NAND, thereby enabling fast data storage and retrieval for real-time processing in connected devices at low cost. These memories are based on phase change, filamentary, magnetic, or ferroelectric mechanisms and often use multi-element materials. They have been extensively explored in 2D capacitor or transistor based devices, but for further density scaling 3D device designs are needed where a conformal deposition technique such as ALD is required. Cell scaling challenges also hold for the traditional DRAM which lead to exploring 3DDRAM integration routes. One viable pathway for scaling implies the replacement of the typical Si-channel based transistor by a deposited semiconductor oxide channel. Ultimate 3DDRAM implementation would require a conformal deposition of that channel.

This presentation reviews key thin film opportunities and challenges, including but not limited to ALD, in a 3D-evolving memory landscape.

9:00am EM1+TF-FrM-3 Patterning Challenges in the Era of Vertical Scaling, *Luciana Meli*, IBM Research Division, Albany, NY **INVITED**

With the end of conventional device scaling, achieving higher compute power has relied on a combination of design and integration innovations, and material breakthroughs to keep up with scaling demands. While traditional dimensional scaling will only continue for the back end of the line, controlling pattern variability and placement remains a critical challenge from a lithography perspective.

Looking ahead, vertical scaling paths will be essential to enhance performance in traditional analog computing and to scale up qubits in quantum computing. This talk will focus on key patterning challenges associated with these vertical scaling pathways, including stacked FETs and chiplet-based architectures, and address opportunities for innovation.

9:40am EM1+TF-FrM-5 Plasma Etch Challenges and Innovations to Enable sub-26nm Pitch L/S Patterning with High-NA EUV, *Nafees Kabir*, Intel Corporation

Extreme ultraviolet (EUV) lithography has been a game changer for the semiconductor industry, enabling tight pitches of 36-40 nm for the 7nm logic technology node. Employing an extremely short 13.5nm wavelength, EUV lithography has surpassed 193i by improving resolution and thus the ability to print tighter features, as well as replacing the complex and expensive multiple-step patterning of 193i with single-patterning. However, despite achieving single-exposure 28nm pitch for the 5nm logic technology node, the current scanner is approaching its resolution limit.

As we prepare to embrace another litho evolution, **high-NA EUV lithography technology** is projected to enable 2nm and beyond logic technology nodes without requiring complex multi-step patterning. The key enabler to improve resolution is the numerical aperture (NA) of the lens. Hence, moving from current **0.33NA to 0.55NA** has the ultimate capability to enable 8nm resolution and patterning 16nm pitch with single-exposure. With this change in NA, the depth-of-focus (DOF) is reduced and pushes us towards the use of **thinner resists** (~20-25nm FT).

This brings us to a new process territory, not only for litho, but also for plasma etch. Need for etch innovation is at a premium to work hand-in-hand to enable pattern transfer of critical features in beyond-2nm logic nodes to further advance Moore's Law.

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In this work, we will share some early innovative plasma etch techniques to demonstrate patterning of basic elements like lines/spaces, contact holes etc. and novel process integration schemes involving Chemically Amplified Resists (CAR) to enable more complex structures with high fidelity.

10:00am **EM1+TF-FrM-6 Area-Selective Deposition with Carborane and Aromatic Self-Assembled Monolayer Blocking Layers**, *Michelle Paquette, R. Bale*, University of Missouri-Kansas City; *B. Garland*, Lehigh University; *S. King*, Intel Corporation; *A. Molder, N. Oylar, S. Pinnepalli*, University of Missouri-Kansas City; *N. Strandwitz, V. Vemuri*, Lehigh University; *T. Vo*, University of Missouri-Kansas City

Area-selective deposition (ASD) is an important strategy in improving the fidelity of and/or reducing the complexity of current multi-pattern pitch-division processes. Dielectric on dielectric (DoD) deposition is of interest for fully self-aligned via flow; however known DoD processes are limited in terms of materials, selectivities, and processing ranges. A common strategy for achieving ASD is to use a blocking layer on the non-growth surface (e.g., a metal) to be able to deposit a target material selectively on the desired surface (e.g., a dielectric). The most well-established blocking layers are self-assembled monolayers (SAMs) based on long alkyl chains, such as dodecanethiol. While these have demonstrated extremely promising results, they do present limitations such as restricted processing windows (e.g., temperature), a typical requirement for solution-phase processing, long exposure times (e.g., 12–48 h), limited stability (temperature, time, chemical), and presence of defects (e.g., pinholes) resulting from disorder or alkyl chain distortions. We investigate two alternative classes of SAMs as blocking layers on metal: carborane thiols and aromatic thiols. Both classes possess several appealing features including the capacity for well-ordered packing (based on 3D symmetry and Van der Waals packing for carboranes and pi-stacking for aromatics), vapor phase deposition, and—importantly—cross-linking through a variety of mechanisms including heat, plasma, and radiation (e.g., UV, e-beam), thus potentially enabling fewer defects, greater stability (leading to wider/more flexible processing windows and/or higher selectivity), as well as the possibility of additional top-down patterning. We investigate the influence of SAM formation (substrate, derivative, deposition conditions, post-deposition treatment) on their resulting composition and structure as well as their blocking capability toward a selection of atomic layer deposition chemistries.

Electronic Materials and Photonics Division

Room B116 - Session EM2-FrM

Emergent Photonic Materials and Devices for Mid-IR Applications

Moderators: *Parag Banerjee*, University of Central Florida, *Erin Cleveland*, U.S. Naval Research Laboratory

10:40am **EM2-FrM-8 Enabling Novel Infrared (IR) Materials for Next-Generation Applications**, *Kathleen A. Richardson*, University of Central Florida, College of Optics and Photonics

INVITED

Technological advances in areas important to industry, defense and society are moving rapidly with requirements to *see and sense* in ways not thought possible before. To realize such advances, new materials with unique function can lead to new components for systems that are smaller, lighter in weight, requisite of less power and lower cost. Security and sensing systems must be versatile to work in a wide range of extreme environmental conditions such as in smoke, fog or in space. Other applications require more robust thermo-mechanical performance metrics, which must be evaluated in trade space to yield a viable solution for more rugged system needs. Materials that transmit light in the infrared portion of the electromagnetic spectrum allows one to 'see' in these regions, often when visible imaging is not possible, but also to serve as windows if they are robust 'enough'. How one transitions viable candidates from lab-scale demonstrators to commercial products takes an understanding of both science and engineering, manufacturability, and prioritization of attributes. This alignment with the end-customer needs must start early in the material design and development process, often well before the actual material solution is fully developed.

This talk reviews general aspects of how infrared glasses for bulk and planar film devices, glass ceramics as gradient refractive index (GRIN) media and alloys for optical phase change (O-PCM) have been designed, developed at prototype scale, and successfully transitioned from the university lab benchtop to the marketplace. These key outcomes suggest a methodology for how this could be done across other candidate optical material systems.

11:20am **EM2-FrM-10 Inverse Piezoelectric Effect in Reverse Biased High-Voltage GaN PN Diodes Observed by In-Situ Biased X-Ray Topography Imaging**, *Andrew Koehler, N. Mahadik*, U.S. Naval Research Laboratory; *M. Liao*, National Research Council Postdoctoral Fellow Residing at U.S. Naval Research Laboratory; *A. Jacobs*, U.S. Naval Research Laboratory; *G. Foster*, Jacobs Inc. Residing at U.S. Naval Research Laboratory; *S. Atwimah, P. Pandey, T. Nelson, D. Georgiev, R. Khanna*, EECs Department University of Toledo; *K. Hobart, T. Anderson*, U.S. Naval Research Laboratory

Next-generation power systems demand increasingly compact and efficient power conversion circuits, which can be delivered by wide bandgap gallium nitride (GaN) technology. Vertical GaN PN junction diodes are fabricated by growing GaN PN epitaxial layers by metal organic chemical vapor deposition (MOCVD) on native GaN substrates. Greater than 800 V reverse blocking voltage is achieved by implementation of nitrogen ion implanted edge termination for electric field management. The termination scheme consists of a hybrid of a shallow implanted junction termination extension (JTE), multiple deeper implanted guard rings (GRs), and implanted isolation that penetrates the PN junction. The implanted nitrogen selectively compensates the P-type doping of the anode layer. 1 mm² discrete diodes were singulated from a wafer and mounted in an open lid custom package with a silver glass die attach, to allow for in-situ biased high resolution X-ray topography (XRT) using $g = [11-20]$ diffraction conditions. Without applied bias, a compressive uniaxial strain of 0.015% is observed, resulting from the die attach process. As illustrated by technology computer aided design (TCAD), the electric field in the diode, under reverse bias, is spread by the edge termination, from the edge of the anode into the termination region, where lattice strain is introduced via the inverse piezoelectric effect. The edge termination effectively operates by reducing the peak electric field at the anode edge; however, the guard rings induce localized nonuniformities in the electric field profile across the termination region, particularly near the surface. The reverse in-situ biased XRT measurements show a nonuniform strain profile in the termination region corresponding to the nonuniform electric field of the GaN diode under reverse bias, with a peak strain near the isolation edge. At a reverse bias of 500 V, the observed piezoelectric induced strain peaked near the isolation implanted edge with a significant (0.32%) amount of strain, which could potentially induce material degradation, causing long-term reliability concerns. In-situ biased XRT imaging can be used as an experimental method to map piezoelectric strain from electric field in GaN, or other piezoelectric material systems to facilitate devices with increased performance and robust operation.

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