## Thin Films
## Room 206 B W - Session TF1-MoM
## Fundamentals of Thin Films I

**Moderators: Jeffrey Elam**, Argonne National Laboratory, **Paul Poodt**, Eindhoven University of Technology, Netherlands

8:15am **TF1-MoM-1 Reduced Oxide Epitaxy at Very High Temperatures*, Joseph Falson,*** Caltech **INVITED**

In this presentation I will discuss epitaxial growth of reduced oxides at very high temperatures and low oxygen pressures, with a specific focus on binary transition metal oxides. We have stabilized a range of high quality films where in addition to injected oxygen, diffusion of anions from the substrate fuels crystal growth and promotes excellent crystallinity. I will also discuss the use of these atomically flat epitaxial layers as building blocks towards complex heterostructures constructed from dissimilar material classes.

8:45am **TF1-MoM-3 High Entropy Oxide Epitaxial Thin Films via Far-from-Equilibrium Synthesis*, Saeed S. I. Almishal,*** *Matthew Furst, Sai Venkata Gayathri Ayyagari,* The Pennsylvania State University*; Pat Kezer,* University of Michigan, Ann Arbor*; Nasim Alem,* The Pennsylvania State University*; Christina Rost,* Virginia Tech*; John Heron,* University of Michigan, Ann Arbor*; Jon-Paul Maria,* The Pennsylvania State University

High entropy oxides (HEOs) are inherently metastable, with properties that are highly sensitive to their thermal history and formation kinetics. Pulsed laser deposition (PLD) stabilizes atomic and electronic configurations far from equilibrium, enabling the exploration of structural and electronic phases inaccessible via conventional bulk synthesis. By precisely tuning growth temperature and rate, PLD directs how materials access metastability and allocate configurational entropy, locally acquiring order within a globally disordered matrix. We exemplify this strategy by growing MgCoNiCuZnO epitaxial thin films, where precise control over substrate temperature and oxygen partial pressure yields up to a 6% variation in the out-of-plane lattice parameter in pseudomorphic thin films across a 200 °C range. By slowing the growth rate or increasing film thickness fivefold, we can induce the formation of two distinct nanostructures: copper-rich nanotweeds and coherent spinel nanocuboids. Incorporating additional cations (e.g., Sc, Cr) facilitates the design of vertically stacked pseudomorphic heterostructures exhibiting exceptional crystalline fidelity and sharp interfaces. Building on these insights, we demonstrate metastable functional oxides—most notably $Srx(Ti,Cr,Nb,Mo,W)O_3$ films—where engineered chemical disorder while maintaining structural order enhances both electron correlation and spin-orbit coupling. Our work demonstrates how entropy-assisted, far-from-equilibrium synthesis via PLD provides transformative opportunities for designing novel functional oxides, significantly expanding the landscape of crystalline materials.

9:00am **TF1-MoM-4 ALD with Alternative Co-Reactants: Which Work, Which Do Not, and Why*, Jay Swarup*[1][2]***, *Robert Mercogliano, James Jensen, Geet Chheda, Robert DiStasio Jr., James Engstrom,* Cornell University

For a number of ALD processes, it is desirable to employ alternative co-reactants to achieve a variety of objectives, which include modifying the temperature window, optimizing the stoichiometry of the thin film, and eliminating undesirable side reactions. Concerning the latter, we have demonstrated that using *t*-BuOH in lieu of $H_2O$ as a co-reactant in ALD with trimethyl aluminum (TMA) results in deposition of a thin film of $Al_2O_3$ that does not oxidize the underlying Co substrate, while use of $H_2O$ does **[1]**. Here we build upon this previous work using a combination of experiments and theory to examine systematically a series of alcohols—primary, secondary and tertiary—as co-reactants with TMA for the ALD of $Al_2O_3$. We compare these results to the benchmark TMA|$H_2O$ process and investigate the role of temperature. We have employed a quartz-crystal microbalance to monitor ALD *in situ* and in real-time, and the deposited thin films have been characterized using XPS. In parallel, we utilized density functional theory (DFT) calculations to identify key reaction intermediates and quantify the kinetics of surface reactions. At a temperature of $T$ = 120 °C we find that none of the 8 alcohols examined result in steady growth of a thin film of $Al_2O_3$. At a temperature of $T$ = 285 °C the situation is quite different, as steady growth is observed, but only by employing tertiary alcohols as co-reactants. Steady growth does not occur with the 6 primary and secondary alcohols examined. For example, concerning structural isomers of $C_4H_9OH$ and $C_5H_{11}OH$, *t*-BuOH and 2-methyl-2-butanol result in steady growth, while 2-butanol and 3-methyl-2-butanol do not. Our calculations using DFT verify the essential role played by the tertiary -OH groups in facilitating the reaction with the chemisorbed species formed in the TMA half-cycle. We find that the important reaction intermediate involves an interaction between an adsorbed alkoxy species with another alcohol, producing -OH(*a*) species. A final issue we addressed concerned the effect of intentionally introducing a small amount of $H_2O$ into the alcohol co-reactants. We find that a mixture of *t*-BuOH and a small amount of $H_2O$ results in steady growth at $T$ = 120 °C, whereas pure *t*-BuOH did not. Similarly, a mixture of *i*-PrOH and a small amount of $H_2O$ results in steady growth at $T$ = 285 °C, whereas pure *i*-PrOH did not. Overall, our study highlights the critical roles played by alcohol order, process temperature, and the influence of small amounts of $H_2O$ impurity on the efficacy of using alcohols as co-reactants in ALD.

[1]J. V. Swarup, H.-R. Chuang, A. L. You, and J. R. Engstrom, ACS Appl. Mater. Interfaces **16**, 16983–16995 (2024).

9:15am **TF1-MoM-5 Enhancing Atomic Layer Deposition Reactor Efficiency for Iridium Thin Films: Balancing Sustainability and Performance in Film Growth*, Jaron Vernal Moon,*** *Timothy J. Gorey,* Los Alamos National Laboratory

Atomic layer deposition (ALD) is a useful technique that enables atomic layer-by-layer growth of conformal films, but the technique is inherently wasteful due to the conventional viscous flow of chemical precursor injection, where the flow stream results in faster film growth at the stream-sample interaction point, reducing coating conformality. This work presents a new, “hold-step” ALD reactor that greatly increases efficiency of conformal film growth while reducing chemical use for improved sustainability. This work specifically focuses on iridium and iridium oxide thin films. By delving deeper into the understanding of the iridium precursor physical properties at temperature, the ALD recipe is tuned to best promote efficient iridium film growth kinetics. By introducing a “hold-step”, the reaction zone is isolated from the vacuum pump during dosing and the pressure is held constant for a set amount of time, resulting in improved film growth as the dosing gases are permitted to diffusively permeate and chemisorb onto embedded surfaces more efficiently. Additionally, characterizing the iridium precursors using techniques such as gas chromatography and thermogravimetric analysis, the ALD reaction can be fine-tuned for effective film growth. By changing from viscous to static flow and better understanding of the precursor kinetics, the total amount of gas required per deposition cycle is substantially reduced. A hold- step reactor design will be presented and compared to traditional ALD reactor designs. For comparison, precursors quantities and the resulting film qualities will be compared. The innovative yet simple design of a hold-step reactor not only enhances film quality but also promotes sustainability by reducing waste gas usage.

9:30am **TF1-MoM-6 Diffusion, Reaction and Thermodynamics of Organic Vapor Phase Infiltration to Overcome Shortcomings of Inorganic Hybridization*, Brian Welch,*** Technion Israel Institute of Technology, Israel*; Bratin Sengupta,* Argonne National Laboratory, USA*; Ruoke Cai,* Technion Israel Institute of Technology, Israel*; Vepa Rozyyev,* Argonne National Laboratory, USA*; Eitan Feldman,* Rice University*; Anil Mane,* Argonne National Laboratory, USA*; Alon Grinberg Dana,* Technion Israel Institute of Technology, Israel*; Jeffrey Elam,* Argonne National Laboratory, USA*; Tamar Segal-Peretz,* Technion Israel Institute of Technology, Israel

Vapor phase infiltration (VPI) enables tailoring of polymeric materials through incorporation of inorganic components. However, the benefits of VPI (also known as sequential infiltration synthesis, SIS) – are often paired with drawbacks such as compromised mechanical stability. Furthermore, the resulting organic-inorganic bonds are often prone to degradation through hydrolysis. To overcome these limitations, we investigate all-organic VPI using step growth molecular layer deposition (MLD) chemistries as a strategy for enhancing polymer properties. We examine the reaction-diffusion kinetics and thermodynamic behavior of three aromatic step-growth polymerization reactions: polyamide, polyurea, and polyimine. Their material growth occurs via MLD at the surfaces of non-absorbing silicon and zirconia. Organic VPI occurs within the bulk of nucleophile-rich polyvinyl alcohol (PVA), but not through physical entrapment in unreactive polystyrene and poly(methyl methacrylate). Using a reaction-diffusion model, we quantify diffusion-limited polyamide and reaction-limited polyurea nucleation behavior in PVA, identifying key parameters: diffusivity,

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

[2] **JVST Highlighted Talk**

reaction rate, and Damköhler number. Unlike inorganic alumina treatment, organic modification enhances dissolution-resistance in PVA, preserving polymer integrity and resisting hydrolysis even in harsh pH 13 solutions. This study demonstrates the potential of all-organic material deposition for synthesizing novel polymers with improved durability and solvent resilience.

9:45am **TF1-MoM-7 Tailoring Ba-Based Thin Films for Security Imaging: Role of $H_2O$ Reactivity and $Al_2O_3$ Supercycle Integration in ALD***, **Adnan Mohammad**, Chi Thang Nguyen, Nuwanthaka Jayaweera, Jacob Kupferberg, Jeffrey W. Elam,* Argonne National Laboratory, USA

Microchannel plate (MCP) electron amplifiers are important components in large-area photodetectors, particularly for security-related applications such as night vision, radiation monitoring, and surveillance. Enhancing their performance and gain depends on advanced thin film coatings with high secondary electron yield (SEY). Barium-containing materials, recognized for their high SEY properties, are highly promising candidates for emissive coatings in MCPs. Atomic layer deposition (ALD) has emerged as a leading fabrication technique for such films, offering advantages in uniformity, pinhole-free morphology, and atomic-scale thickness control at low processing temperatures. However, despite ALD's potential, research on barium-thin films via this method remains under-explored. Notably, no prior work has investigated ALD-synthesized barium-based coatings in MCPs, presenting a significant opportunity to bridge this gap.

In this study, we demonstrate the thermal atomic layer deposition (ALD) of barium-containing thin films using bis(tri(isopropyl)cyclopentadienyl)barium ($Ba(iPr_3cp)_2$) as the barium precursor and water ($H_2O$) as the co-reactant. We further investigate the structural and functional impact of incorporating alumina via super-cycle deposition within the $Ba(iPr_3cp)_2/H_2O$ process. The $Ba(iPr_3cp)_2$ precursor was vaporized at 175°C, and depositions were performed in a hot-wall reactor at 250°C under a pressure of ~1.2 Torr. Systematic saturation studies were conducted to optimize precursor temperature, dose time, purge duration, and co-reactant exposure. Real-time thin film growth was monitored using in-situ ellipsometry, which enabled rapid saturation analysis while providing valuable insights into surface reactions during each ALD cycle.

The barium-containing films were characterized using X-ray photoelectron spectroscopy (XPS) for chemical composition, X-ray diffraction (XRD) for crystalline structure, X-ray reflectivity (XRR) for density, and atomic force microscopy (AFM) for surface topography. Moving forward, we aim to integrate ALD-grown barium layers onto microchannel plate (MCP) substrates and systematically evaluate their resistance, gain, and temporal stability. These metrics will directly assess secondary electron yield (SEY) performance, validating the material's potential as a high-SEY coating to enhance MCP efficiency.

## Thin Films
## Room 206 B W - Session TF2-MoM
## Characterization of Thin Films

**Moderators: Joseph Falson**, Caltech, **John Hennessy**, Jet Propulsion Laboratory (NASA/JPL)

11:00am **TF2-MoM-12 Data Science Tools to Disentangle Large Electron Diffraction Datasets of Thin Films***, **Matthias Young**, Andreas Werbrouck, Andrew Meng, Dilan Gamachchige, Indeewari Herathlage, Nikhila Paranamana, Xiaoqing He,* University of Missouri

Historically, the thin film community has been largely driven by process-property understanding, and we have had limited access to deep understanding of the atomic-scale structure of vapor-deposited thin films. This arises from challenges in measuring the atomic structure of these films due to (1) their amorphous, polycrystalline, and defective structures, and (2) the ultrathin film thicknesses, often with gradients in composition and structure in the x-y and z directions. Prior work has established an understanding of how the structure of vapor-deposited thin films evolves during growth using bulk measurements such as infrared spectroscopy, synchrotron diffraction, and nuclear magnetic resonance, or surface sensitive measurements such as X-ray photoelectron spectroscopy. However, these approaches struggle to provide position- or depth-dependent atomic structure information, especially at sub-nanometer length scales. In recent years, our group has employed transmission electron microscopy (TEM) diffraction to measure the atomic structure of atomic layer deposition (ALD) films with high spatial resolution across nanoscale interfaces. However, even with TEM, the presence of multiple phases and orientations that are distributed in different amounts throughout the film volume and co-located in the beam path in each diffraction image make interpretation challenging. Here, we employ a data science algorithm known as non-negative matrix factorization (NMF) to identify the unique component diffraction signals and map their locations throughout ultrathin interfacial volumes. To facilitate this on the large volume of data present from a series of 2D diffraction patterns collected over a rastered 2D measurement area during scanning TEM (4D-STEM), we report the use of QR decomposition for randomized non-negative factorization as well as feature reduction through superpixel clustering. Together the speed-ups provided by these approaches allow for the rapid processing of high volumes of TEM data, enabling component isolation and spatial mapping for several gigabytes of electron diffraction data in minutes on a laptop compared to the hours required without these acceleration approaches. This allows us to quickly distill high volumes of data down to meaningful insights with low computational overhead, promising to enable more rapid discovery and innovation in the thin film community.

11:15am **TF2-MoM-13 A Novel *A*pproach to Study EUV and BEUV Photoresist Sensitivity through Real-time µXPS***, **Peter Sun**, Samuel Tenney, Chang-Yong Nam, Jerzy Sadowski,* Brookhaven National Laboratory

Extreme ultraviolet (EUV) and beyond extreme ultraviolet (BEUV) lithography can achieve sub-10 nm features in semiconductor manufacturing. These nanoscale patterns require photoresists to be highly sensitive to EUV and BEUV conditions. One of the photoresist candidates are polymethyl methacrylate (PMMA) based hybrid photoresists with vapor phase infiltrated (VPI) inorganic materials.

The sensitivity of the photoresists depends on photo absorption efficiency, secondary electron generation, and material degradation. Currently, sensitivity studies mainly focus on characterizing developed films, an approach that cannot decouple photoresist sensitivity and developer sensitivity. To isolate the photoresist sensitivity, a method to study these photoresists' in situ exposure behavior before development is needed.

This report presents a novel approach to studying photoresist sensitivity through in situ real-time low-energy electron/photoemission electron microscopy (LEEM/PEEM) and micro-spot X-ray photoelectron spectroscopy (µXPS). In particular, we model the time-dependent chemical change and the charging behavior of the photoresists under X-ray exposures at 92 eV and 400 eV. We show the approach is reliable in determining the PMMA and its VPI hybrids' sensitivity to EUV and BEUV conditions. This approach will allow the study of a broader range of EUV and BEUV photoresist candidates and assist in next-generation photoresist and developer selection.

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11:30am **TF2-MoM-14 Stoichiometric Determination in Thin Films: A Study of $BaTiO_3$***, **Peter Dickens**, Melissa Meyerson, Mark Rodriguez, Clare Davis-Wheeler, Jonathan Heile, William Wampler, Christian Harris, Brianna Klein,* Sandia National Laboratories

Thin films are essential in modern technology, providing unique properties for electronic, sensor, and optical applications. As more complex alloys and compounds are integrated onto devices, the need to effectively characterize material composition becomes increasingly important. To surmount this hurdle, many different methods are utilized throughout literature with XRF, XPS, and EDX being prime among the reported methods; however, it is common for there to be little to no discussion on the analysis, nuances, and accuracy of the technique used. These issues are further exacerbated by the common availability of black box analysis associated with each of these techniques leading to reports and conclusions based on imprecise analysis.

In this presentation we use BaTiO3 as a case study material to compare each of the common compositional methods. We report on the determination of the Ba/Ti atomic ratio in four thin films deposited by sputter deposition under conditions to produce a range of stoichiometries. We directly compare analysis produced from X-ray Fluorescence (XRF), Rutherford Backscatter Spectroscopy (RBS), Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES), X-ray Photoelectron Spectroscopy (XPS), and Wavelength Dispersive Spectroscopy (WDS). Discussion is focused on accuracy of each technique and nuances related to each method and the analysis.

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SAND2025-04533A

11:45am **TF2-MoM-15 Advanced Characterization of Inorganic and Organic Liners for Through Vias in Glass Packages***, Meghna Narayanan,* *Mohan Kathaperumal, Mark Losego,* Georgia Institute of Technology, USA

Electronic packaging technology is evolving towards advanced substrates, including glass, to overcome limitations posed by traditional organic substrates. Glass packaging offers low dielectric loss, high modulus, low and tunable coefficient of thermal expansion (CTE), enhanced thermal stability, high I/O density, and reduced warpage. However, fully adopting glass packaging technology still faces several hurdles, including metal adhesion, stress management, and a full understanding of long-term reliability. The CTE mismatch between glass and copper (5 to 15 ppm/°C) leads to reliability issues such as glass and through-glass via (TGV) cracking, copper via protrusion, and delamination. We aim to address the glass and TGV cracking by introducing an organic or inorganic liner inside the TGV to act as a stress buffer, lowering the propensity for TGV electrode failure. In this study, we will describe TGV substrates coated with different liners – Parylene C, $SiO_2N$, $SiO_3N$, AZO (Aluminium-Zinc oxide), and Parylene C+AZO, obtained through different methods of deposition. The foremost step is to characterize if the liner is conformally coating the 100 µm diameter via. Conformal coating is essential to mechanical performance and even electroplating through the entire depth of the TGVs. A non-uniform liner coating will lead to an uneven Ti-Cu seed layer prior to electroplating of copper. Since the liner can be 0.1 to 5 µm thick, cross-sectioning is inadequate for post-plating liner inspection. Non-destructive methods for evaluating these coatings would also be of value to research and development, as well as in-line process monitoring. We have evaluated the effectiveness of several methods. In this work, two advanced techniques—two-photon imaging and micro-computed tomography (microCT)—are used to assess liner uniformity and measure thickness. Two-photon imaging is particularly effective for fluorescent materials like Parylene C and SiO2N, enabling visualization and thickness measurement within TGVs. The thickness of Parylene C is measured to be 5.6 µm (expanding to 8.7 µm near the surface), and Parylene C+AZO is measured to be 1.87 µm (expanding to 2.8 µm near the surface). Although AZO and $SiO_2N$ are fluorescent, the nanoscale thickness (< 100 nm) is challenging to measure due to the resolution of the tools. The paper will propose additional metrology tools and show preliminary attempts to measure such nanoscale thicknesses. We will also show preliminary results on plating the liner-coated TGVs to assess their performance in mitigating crack formation upon thermal cycling.

## Thin Films
## Room 206 B W - Session TF1-MoA
## Thin Films for Energy I

**Moderators: Blake Nuwayhid**, Naval Research Laboratory, **Matthias Young**, University of Missouri

2:00pm **TF1-MoA-3 Enabling Scalable Sustainable Energy Devices via Spatial Atomic Layer Deposition*, Paul Poodt,*** SparkNano and Eindhoven University of Technology, Netherlands **INVITED**

Atomic Layer Deposition is a key enabler for next-generation energy storage and conversion technologies, offering unmatched control over film thickness and composition with excellent conformality on complex and porous surfaces. However, many applications—such as electrolysis and batteries—require high-throughput, low-cost processing, making Spatial ALD (sALD) an attractive solution.

We present recent advances in sALD for two key applications: electrocatalyst coatings for proton exchange membrane water electrolysis (PEMWE) and LiF passivation layers for Li-ion battery electrodes.

PEMWE is a leading method for green hydrogen production. Current systems rely on Ir- and Pt-based electrocatalysts, but the high cost and scarcity of these materials pose scalability challenges. ALD enables ultrathin, conformal catalyst layers with atomic-level control, allowing significant reductions in noble metal usage. We demonstrate sALD of Ir- and Pt-based materials at full PEM stack scale. These coatings achieve 10–100× lower Ir loadings than current standards while maintaining excellent stability under accelerated stress tests.

In Li-ion batteries, LiF has emerged as a promising solid-electrolyte interphase (SEI) component due to its chemical robustness and wide electrochemical stability window. Conventional ALD of LiF often requires high temperatures and undesirable sources of fluorine. We introduce a plasma-enhanced sALD process using a new lithium precursor to deposit pure, crystalline LiF at 100–200°C—compatible with Li-metal anodes and other sensitive substrates. The films exhibit high growth rates, excellent conformality, and are free of oxygen and carbon. Examples of significant improvements in capacity retention will be shown.

Finally, we address the critical role of precursor utilization efficiency in sALD. Through combined experiments and modeling, we show how process parameters—such as surface area, aspect ratio, throughput, temperature, and pressure—can be tuned to minimize precursor waste. Efficient precursor use is essential for the cost-effective and sustainable scaling of ALD in electrochemical device manufacturing.

2:30pm **TF1-MoA-5 Manufacturing-Scale Powder Atomic Layer Deposition for Battery Applications*, Arrelaine Dameron,*** Forge Nano Inc **INVITED**

Historically Atomic layer deposition (ALD) has been regarded as a lab-only process, disregarded as too expensive and an unrealistic process for commercial adoption outside of semiconductor manufacturing. However, several methods for high volume manufacturing have been developed over the last decade, making ALD on powders affordable as a material-upgrading technique. Forge Nano has patented, constructed, and demonstrated the highest throughput ALD capability in the world, unlocking new potential for lower cost integration of ALD into products. ALD is a well utilized platform technology for powders, porous particles, and high-surface area objects that has been widely demonstrated throughout the literature. Fundamentally, ALD on powders or any high surface area surface is the same as on flat surfaces -- if the chemistry is self-limiting, the precursors can be kept separate and supplied at a concentration to saturate the available surface area, the thin film growth will be controlled and uniform. In practice, the very high surface area, long diffusion pathways, and complexities of gas solids mixing bring a few additional challenges not usually encountered during lab-scale ALD.

Commercial adoption of EVs requires that we overcome consumer angst around battery range by enabling fast charge and increasing specific capacity, while also significantly decreasing cost ($/kWh). Achieving these objectives requires higher energy density and higher charge rate operation of high-capacity cathodes and anodes. It also requires that we standup a robust supply chain for battery materials and implement process intensification to minimize manufacturing costs. The major challenge of high-capacity cathode materials paired with low-cost graphite or Si/graphite anodes is their propensity for transition metal dissolution and crossover, and gas generation, which stems from electrochemical decomposition of the electrolyte solvent at electrode-electrolyte interfaces. These degrade battery performance and increase safety risk.FN has developed ALD coatings that can improve anode and cathode materials.

This talk will highlight the benefits of nano-engineering the surface of anode and cathode materials for lithium-ion battery cell development and manufacturing considerations when scaling those solutions for battery production.

3:00pm **TF1-MoA-7 Thin Film Solid-State Electrodes for Electrochemical-Mechanical Coupling Experiments*, M. Florencia Petracci,*** *Bhuvsmita Bhargava, Yueming Song, David Stewart, Taeho Jung,* University of Maryland, College Park*; Alec Talin,* Sandia National Laboratories*; Gary Rubloff, Paul Albertus,* University of Maryland, College Park

Measuring and studying the coupling between mechanical stresses and electrochemical responses in solid state batteries can be challenging due to the presence of several irregular interfaces, and to the non-uniform stress distributions present at them. It is essential to understand this coupling since these mechanical stresses and strains, resulting from fabrication, volume changes from ion insertion and extraction and applied operating pressures, can affect the thermodynamics, kinetics and transport mechanisms in batteries and thus impact their performance.

Our platform, which consists of thin-film electrode samples with mechanically planar interfaces in lateral configurations, and the use of a flat platen connected to a Nanoindenter, allows us to apply controlled uniaxial forces to single electrode interfaces [1]. This platform is used to directly measure the effect that applied stresses have on interfacial equilibrium potentials.

In this presentation we will introduce our platform, including the fabrication of our thin-film $V_2O_5$ cathodes through reactive sputtering [2] on LATP solid electrolyte substrates with a Lithium metal anode, our testing and characterization protocols, as well as our results showing clear coupling between applied mechanical loads and open-circuit voltage. This coupling varies with lithiation state of the sample due to changes in the partial molar volume of Lithium in the $V_2O_5$. The partial molar volume of Lithium in $V_2O_5$ obtained from this platform falls into the range between 2.5 to 5 $cm^3$/mol, which is consistent with what has been observed for other intercalation materials[3].

References:

[1] Song, Y., Bhargava, B., Stewart, D. M., Talin, A. A., Rubloff, G. W., & Albertus, P. (2023). Electrochemical-mechanical coupling measurements. *Joule*, 7(4), 652-674.

[2] Warecki, Z., Ferrari, V. C., Robinson, D. A., Sugar, J. D., Lee, J., Ievlev, A. V., ... & Talin, A. A. (2024).Simultaneous Solid Electrolyte Deposition and Cathode Lithiation for Thin Film Batteries and Lithium Iontronic Devices. *ACS Energy Letters*, 9(5), 2065-2074

[3] Koerver, R., Zhang, W., De Biasi, L., Schweidler, S., Kondrakov, A. O., Kolling, S., ... & Janek, J. (2018). Chemo-mechanical expansion of lithium electrode materials–on the route to mechanically optimized all-solid-state batteries. *Energy & Environmental Science*, 11(8), 2142-2158

3:15pm **TF1-MoA-8 Mapping Lithium Diffusion in Thin-Film $V_2O_5$ Using Raman Spectroscopy*, Daniel MacAyeal,*** University of Vermont*; Leopoldo Jose Tapia-Aracayo,* University of Maryland, College Park*; Spencer Caverly,* University of Maryland*; David Stewart, Gary Rubloff,* University of Maryland, College Park*; Alexander Kozen,* University of Vermont

Understanding the lateral diffusion of lithium in thin-film solid state battery (SSB) materials is critical to improving SSB performance, stability, lifespan, and architecture. Using model test structures of sputtered annealed- and unannealed-$V_2O_5$/LiPON, we use Raman spectroscopy peak shifts to map Lithium concentration in $V_2O_5$/$VO_x$. We evaluate the diffusion of lithium from LiPON layers into thin-film Vanadium Oxide, measure the impact of different sputter deposition process conditions on lateral lithium diffusion into crystalline and amorphous metal oxide films. We confirm experimental results with simulations, exploring both potential-driven diffusion and Fickian diffusion as possible mechanisms for Lithium transport. Lastly, we will discuss the important implications of the lateral spacing limitations of clustered SSB devices due to lateral diffusion and propose architectural design rules based on this diffusion behavior for optimized device performance.

## Thin Films
## Room 206 B W - Session TF2-MoA

## Thin Films for Energy II

**Moderator: Alexander Kozen**, University of Vermont

4:00pm **TF2-MoA-11 Interface Engineering for the Highly Efficient Antimony Chalcogenides Thin Film Energy Devices*, Feng Yan,*** Arizona State University **INVITED**

Antimony chalcogenide ($Sb_2X_3$, X=S, Se, Te) thin film solar cells have garnered significant interest due to their optimal bandgap, high absorption coefficient, and earth-abundant constituent elements. Interface engineering plays a pivotal role in optimizing the performance of these solar cells, as the interfaces between different layers critically influence charge carrier dynamics. This talk focuses on systematically investigating and engineering interfaces in $Sb_2X_3$-based thin film solar cells to enhance their efficiency and stability. Precise control over interface properties was achieved by employing techniques such as sputtering and chemical bath deposition (CBD). The introduction of buffer layers, passivation treatments, and surface modifications were explored to mitigate recombination losses and improve charge extraction. Advanced characterization methods including X-ray photoelectron spectroscopy (XPS), were utilized to analyze the interfacial properties and their impact on device performance. The findings highlight the critical importance of interface quality and the potential of tailored interface engineering to unlock higher efficiencies in antimony chalcogenide thin film solar cells. This work provides a pathway for further optimization and commercial viability of Sb2X3 solar cells, contributing to the advancement of sustainable photovoltaic and photoelectrochemical technologies.

4:30pm **TF2-MoA-13 Developing R32 Barium Nickelate Thin Films for Catalysis*, Ian Graham,*** Georgia Institute of Technology*; Kayla Chuong, Anna Österholm, Lauren Garten,* Georgia Institute of Technology, USA

The oxygen evolution reaction (OER) is the rate limiting step inhibiting the production of fuel from water.[1,2] Barium nickelate (BNO) is a promising catalyst, due to a tunable oxygen stoichiometry without significant structural changes to the crystalline phases. Tuning oxygen stoichiometry in transition metal oxides can modulate the band structure and increase catalytic activity.[3] The *R*32 phase of BNO is proposed to exhibit increased OER catalytic activity due to a theoretically predicted $e_g$ orbital filling of Ni near the optimal value of 1.2 for OER.[1] However, the range of stoichiometries, and therefore Ni oxidation states, that the *R*32 phase of BNO can exhibit are not yet known.

Here, we stabilized the *R*32 phase of BNO in thin films using a $BaNi_{0.93}O_{2.68}$ target by pulsed laser deposition (PLD) on (0001) $Al_2O_3$ substrates. The films were deposited at a substrate setpoint temperature of 400 °C, oxygen partial pressures ranging from 0.012-0.091 mbar, and a laser fluence of 2.5 $J/cm^2$. X-ray diffraction shows that the films are solely (100) oriented and only the *R*32 phase is observed over this range of partial pressures. Energy dispersive X-ray spectroscopy reveals that the film stoichiometries range from $BaNi_{1.10}O_{2.26}$ to $BaNi_{1.03}O_{2.14}$. The range of stable oxygen stoichiometries is further increased by post annealing in an oxygen atmosphere beyond those available by PLD. X-ray photoelectron spectroscopy indicates the presence of $Ni^{2+}$, $Ni^{3+}$, and $Ni^{4+}$. Four-point probe measurements show an increase in resistivity with increasing oxygen stoichiometry; decreasing oxygen stoichiometry to $BaNi_{1.03}O_{2.14}$ resulted in a conductivity of 0.161 S/m. Then films were deposited on conductive (111) $Nb{:}SrTiO_3$ substrates for impedance spectroscopy, dielectric, and piezoelectric measurements. The piezoelectric response was measured using laser doppler vibrometry in an $e_{11,f}$ wafer flexure system. Impedance spectroscopy results further show the role of oxygen vacancies migration on the electronic and ionic conductivity.

References

1) Lee et al., *J. Am. Chem. Soc.* **2016**, 138 (10), 3541–3547.

2) Plevová et al., *Journal of Power Sources* **2021**, 507, 230072.

3) Wang et al., *ACS Catal*. **2018**, 8 (1), 364–371.

4:45pm **TF2-MoA-14 Nano Layers, Tera Goals : Atomic Layer Deposition of Ruthenium for the future Hydrogen Economy*, Swapnil Nalawade,*** *Shyam Aravamudhan, Mengxin Liu, Dhananjay Kumar,* North Carolina A&T State University

Atomic layer deposition (ALD) enables angstrom level control over material synthesis, making it a powerful platform for engineering catalytic thin films. In this study, we report the deposition of ultrathin Ruthenium (Ru) films on TiO2 substrates with (100),(101) and (110) orientations via thermal ALD using organometallic precursor ($Ru(ETCP)_2$) and oxygen as co-reactant. The process yield conformal, uniform and highly crystalline as confirmed by X ray photoelectron spectroscopy (XPS) and X ray diffraction (XRD). XRD showed hexagonal closed packed structure and XPS confirmed the binding energy of $Ru3d_{5/2}$ is associated with $Ru^{(0)}$. Electrochemical evaluation demonstrates hydrogen and oxygen evolution reactions in 0.1 M $H_2SO_4$, achieving enhanced catalytic activity for Ru on TiO2(110) which also exhibited lower charge transfer resistance in EIS plot. Tafel slopes also highlighted different kinetics for different Ru films. To understand surface chemistry and guide future refinement, first principles density functional theory (DFT) calculations will be employed to explore reaction mechanisms to unravel the energetics and rate limiting steps during growth of Ru films. DFT will help in understanding precursor-ligand decomposition, oxygen interaction and surface termination dynamics during the ALD cycle. This integrated experimental-computational approach illustrates how nanoengineered Ru films can play pivotal role in enabling next generation clean energy infrastructure to achieve terawatt scale hydrogen production.

5:00pm **TF2-MoA-15 Sputter Deposition of Composite Membranes for High Performance Hydrogen Purification*, Cameron Burst,*** Colorado School of Mines*; Thomas Fuerst,* Idaho National Laboratory*; Doug Way, Colin Wolden,* Colorado School of Mines

Ultrahigh purity hydrogen is essential in many fields including semiconductor processing, fuel cells, and fusion energy.Palladium-based foils offer high flux and perfect selectivity for hydrogen purification, but are prohibitively expensive for many applications. BCC metals like vanadium (V) and niobium (Nb) are ~600X less expensive and offer an order of magnitude greater hydrogen permeability, but require the application of a catalyst to efficiently dissociate and recombine molecular hydrogen and protect V and Nb from uptake of nonmetal impurities. In this work sputter deposition is used to fabricate composite membranes to unlock the full potential of BCC metal foils. Pd is a great catalyst, but will rapidly interdiffuse with BCC metals. In the first strategy we deposit a TiN interdiffusion barrier between Pd and the underlying V foil.TiN was deposited via reactive sputtering, and films with the desired (200) orientation were obtained in the metallic regime at 400 °C with the application of a 200 V bias. The permeability of thin-film TiN was determined with palladium-based sandwich structures. TiN layers up to 10 nm resulted in a minimal decrease in flux (~20%) relative to a freestanding PdCu foil, which was attributed to the interfacial resistance. Composite Pd|TiN|V|TiN|Pd membranes exhibited permeability values up to three times greater than pure palladium, exhibiting stability at 450 °C for over 100 h. However, the membranes were unstable at 500 °C, which was attributed to the instability of the thin Pd layer and loss of catalytic activity. The second strategy involved using sputter–deposited $TiO_2$ as a catalyst layer. It was found that anatase $TiO_2$ was an excellent catalyst for $H_2$ activation, producing composite membranes that achieved theoretical permeability at 500 ºC.After 20 hours of operation these membranes begin to display a slow decline in performance. Extensive materials characterization techniques are employed to understand the underlying reasons driving performance and to further improve the stability of these composite membranes.

## Electronic Materials and Photonics
## Room 207 A W - Session EM1+AP+CPS+MS+PS+QS+SM+TF-TuM

### Emerging Frontiers in Quantum Materials and Devices
**Moderator: Mollie Schwartz**, MIT Lincoln Laboratory

8:30am **EM1+AP+CPS+MS+PS+QS+SM+TF-TuM-3 Rapid, Atomic-Scale Smoothing of GaSb(111)A Surfaces During Molecular Beam Epitaxy**, ***James Rushing***, *Paul Simmonds,* Tufts University

InAs/Ga(In)Sb quantum wells (QWs) with a broken gap band alignment can behave as a quantum spin hall insulator (QSHI) with an insulating bulk and topologically protected helical edge states [1-2]. QSHIs could be a key component in spintronic and topological quantum computing applications [2-3]. Producing a topological phase transition in InAs/Ga(In)Sb QWs requires precise control of QW thickness, composition and quality, particularly at the heterointerfaces. Additionally, our calculations suggest QWs grown on (111) surfaces could provide benefits over (001) due to the higher symmetry and out-of-plane polarization effects of this surface.

While exploring the MBE growth of InAs/Ga(In)Sb QW heterostructures on GaSb(111)A, we discovered an exciting and confounding phenomenon that seems to be unique to crystal growth on III-Sb(111)A surfaces. Ga(In)Sb(111)A frequently exhibits an extremely rough morphology characterized by pyramidal peaks covering the entire surface. We show that rough III-Sb surfaces (pyramidal features >70nm in height; rms roughness >10nm), can be smoothed to atomically flat surfaces (<3nm height features; <0.5nm rms roughness) in a matter of seconds by exposing them to an arsenic over-pressure. We first observed this phenomenon when rough GaInSb(111)A surfaces became atomically flat after capping with just 8nm of InAs. After reducing the thickness of this InAs layer to a single monolayer and still observing he same surface smoothing effect, we found that we could achieve almost identical results by simply exposing the rough GaSb(111)A to an arsenic flux. These results suggest that arsenic is the primary mover in these profound morphological changes. Our recent results show that the smoothing can be accomplished with $As_4$ or $As_2$, and with a wide range of arsenic beam equivalent pressures, from $5\times10^{-7}$ to $1\times10^{-5}$ Torr.

We will describe our efforts to gain control and understanding of this phenomenon through the modulation of arsenic exposure time, flux, and terminating III-Sb material. This powerful new MBE technique will allow us to reliably achieve smooth heterointerfaces in (111)-oriented InAs/Ga(In)Sb QWs for novel, high-quality QSHIs. More broadly, we believe that this approach will enable the growth of a wide array of III-Sb-based nanostructures on (111)A surfaces for other electronic and photonic applications.

1. Krishtopenko and Teppe. *Science Advances* **4**, eaap7529 (2018)
2. Avogadri et al. *Physical Review Research* **4**, L042042 (2022)
3. Du et al. *Physical Review Letters* **119**, 056803 (2017)

8:45am **EM1+AP+CPS+MS+PS+QS+SM+TF-TuM-4 Benchmarking Different NbTiN Sputtering Methods for 300 mm CMOS-compatible Superconducting Digital Circuits**, *Adham Elshaer*[1], ***Jean-Philippe Soulié***, *Daniel Perez Lozano, Gilles Delie, Ankit Pokhrel, Benjamin Huet,* IMEC Belgium*; Margriet J. Van Bael,* KU Leuven and Imec, Belgium*; Daan Buseyne,* KU Leuven, Belgium*; Blake Hodges, Seifallah Ibrahim, Sabine O'Neal,* Imec USA*; Zsolt Tökei,* Imec Belgium*; Anna Herr, Quentin Herr,* Imec USA

The NbTiN films presented here are CMOS-compatible and were developed for metallization purposes in superconducting digital circuits [1-5]. Those circuits use NbTiN for Josephson junctions and capacitors electrodes, as well as for wiring. Superconducting digital circuits initially relied on Nb in the early days. NbTiN is a better candidate/replacement due to its higher thermal budget and better chemical stability [1-5]. In this study, the properties of superconducting NbTiN thin films deposited using two different sputtering methods have been compared. One method used multiple targets (MT) co-sputtering (Nb and Ti targets), while the other used a NbTi single target (ST). Benchmarking metrics used for comparison include: superconducting, electrical, as well as morphological properties. All films show a high Tc, ranging from 13.3 K to 15.1 K. Compared to MT, ST NbTiN films showed consistently lower resistivity and better sheet resistance (Rs) wafer-level uniformity (49 points wafer-map). For instance, 50 nm MT film had a Rs relative standard deviation (Stddev%) of 15.5%, while for the ST NbTiN films, Rs Stddev% showed a 2-fold improvement at 7.8%. Upon annealing of the ST NbTiN films at 650℃, the Rs uniformity further improved, reflected by a lower Stddev% at 4.5%. AFM data show similar results for MT and ST films, ~1.07 nm and 1.09 in the center and 0.73 nm and 0.71 nm at the edge of the wafers, respectively. Furthermore, XRD theta-2theta scans have been performed showing the 200 and 111 peaks for NbTiN orientations. Results show that the MT and ST films have different/signature 200/111 peak intensity ratios for the as deposited films. ST NbTiN films have a lower 200/111 peak ratio. However, after annealing at 650℃, the ST films 200/111 peak ratio increases, and surpasses that of the MT NbTiN films. This change suggests a change in the ST film disorder and grain size after annealing. The impact of the ST NbTiN film thickness on properties has also been studied. The Tc shows an increase as a function of thickness, from 9.6 K for 7 nm, to 14.3 K for 50 nm, up to 14.9 K for 200 nm films. Certainly, the ability to tune the superconducting properties of NbTiN, makes them appealing from a stack engineering perspective. Both MT and ST NbTiN properties can be tailored using deposition conditions such as: power, partial pressure and post deposition annealing [3]. However, MT NbTiN films 300 mm wafer-level Rs non-uniformity represents a limiting factor for scaling superconducting devices. Annealed NbTiN ST films on the other hand, show a 3.4-fold Rs wafer uniformity improvement while maintaining properties tunability.

9:00am **EM1+AP+CPS+MS+PS+QS+SM+TF-TuM-5 Controlling the Properties of Epitaxially Grown Topological Semimetals**, ***Kirstin Alberi,*** National Renewable Energy Laboratory **INVITED**

Three dimensional topological semimetals (TSMs) exhibit a wide range of interesting properties, including high carrier mobility, large magnetoresistance, anomalous transport behavior, broadband optical absorption and non-linear optical responses. Epitaxial thin film synthesis offers a practical platform for manipulating composition, defects and disorder in these materials, offering a window into approaches for manipulating their properties. In this talk, I will discuss insights into the relationships between structure and composition and the resulting properties revealed through careful control of growth conditions. Focused examples include the impact of point defects and impurities on electron transport in the Dirac TSM $Cd_3As_2$ and the formation and behavior of domain boundaries in the Weyl TSM TaAs.

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9:30am **EM1+AP+CPS+MS+PS+QS+SM+TF-TuM-7 Photon Down-Conversion of Yb-Doped CsPb(Cl1-xBrx)3 to Low-bandgap Metal Halide Perovskites**, ***Yutong Ren***[2], Princeton University*; Igal Levine,* The Hebrew University of Jerusalem, Israel*; Dan Oron, David Cahen,* Weizmann Institute of Science, Israel*; Antoine Kahn,* Princeton University

Quantum cutting represents a transformative strategy to mitigate thermalization losses that typically occur when high-energy photons are absorbed by semiconductors.[1,2] Recent advances have extended this concept from rare-earth doped crystals to semiconductor–rare-earth hybrid systems, particularly those utilizing halide perovskite absorbers, thereby exploiting their exceptional optoelectronic properties.

In this study, we focus on Ytterbium (Yb) -doped $CsPb(Cl_{1-x}Br_x)_3$, a metal halide perovskite that absorbs visible light and exhibits intense near-infrared (NIR) photoluminescence—a clear signature of efficient quantum cutting. Upon excitation with visible light, the doped perovskite converts the absorbed energy into two NIR photons, with the emission energy closely matching the optimized bandgap of a Sn–Pb based perovskite absorber. This spectral alignment is critical for enabling effective energy transfer between the quantum cutting layer and the absorber.

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[1] **JVST Highlighted Talk**

[2] **JVST Highlighted Talk**

Our investigation focuses on elucidating the structural and electronic properties of the interfaces between Yb-doped $CsPb(Cl_{1-x}Br_x)_3$ and Sn–Pb based perovskite films. By employing a suite of advanced spectroscopic techniques—including ultraviolet photoelectron spectroscopy, inverse photoemission spectroscopy, time-resolved photoluminescence (tr-PL), and time-resolved surface photovoltage (tr-SPV)—we systematically examine how the quantum cutting layer, the absorber layer, and their interfacial region collectively influence energy transfer efficiency. In particular, the complementary tr-PL and tr-SPV analyses unambiguously determine the dominant interfacial charge transfer and recombination processes, and thus gain control over the interfacial charge transfer. By integrating Yb-doped $CsPb(Cl_{1-x}Br_x)_3$ with customized Sn–Pb perovskite absorbers, our approach shows promise for pushing the boundaries of conventional efficiency limits while also offering a cost-effective strategy for enhanced energy conversion.

1. Wegh, R. T. et al. Quantum cutting through downconversion in rare-earth compounds. *J. Lumin.* **87–89**, 1017–1019 (2000).

2. Kroupa, D. M. et al. Quantum-cutting ytterbium-doped $CsPb(Cl_{1-x}Br_x)_3$ perovskite thin films with photoluminescence quantum yields over 190%. *ACS Energy Lett.* **3**, 2390–2395 (2018).

9:45am **EM1+AP+CPS+MS+PS+QS+SM+TF-TuM-8 Molecular Beam Epitaxy Growth of $InAs_{1-x}Bi_x$ on GaSb for Topological Insulating States***, **Merve Baksi**, James Rushing, Xikae Xie, Avery Hanna, Larry Qui, Ekow Williams, Paul J. Simmonds,* Tufts University

Incorporation of bismuth (Bi) into III-V semiconductors has attracted significant interest not only for its ability to extend infrared optoelectronic applications across a wide spectral range but also for its potential to induce topologically protected surface states, which could form the foundation for certain quantum computing technologies [1].

Motivated by the small inverted band gap that can be induced in InAs/GaSb quantum wells (QWs) [2], we propose engineering the band structure and inducing the edge states through Bi incorporation into InAs layers. This enhancement is expected to improve robustness against thermal fluctuations, making the material viable for room temperature applications as opposed to the topological HgTe/CdTe QW system with a temperature dependent band gap [3].

Theoretical studies predict that $InAs_{1-x}Bi_x$ quantum wells exhibit a topological insulating state when the Bi composition reaches $x \approx 0.15$, with an estimated inverted gap of approximately 30 meV [1]. Given these predictions, InAsBi emerges as a promising candidate for realizing two-dimensional topological insulators (2D TIs). However, achieving such high Bi incorporation remains challenging due to the significant miscibility gap and the limited solubility of Bi in III-V materials [4].

In this work, we investigate the molecular beam epitaxy (MBE) growth of InAsBi on GaSb substrates, focusing on optimizing Bi incorporation and structural quality. By leveraging MBE growth techniques, we aim to systematically control Bi incorporation and assess its impact on electronic and structural properties of InAsBi in reduced dimensions. Our findings will contribute to the advancement of III-V-based topological materials and their potential integration into future quantum devices.

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## Electronic Materials and Photonics
## Room 207 A W - Session EM2+AP+QS+TF-TuM

### Evolution of Materials and Devices for Energy Harvesting and Conversion

**Moderators: Seth King**, University of Wisconsin - La Crosse, **Parag Banerjee**, University of Central Florida

11:00am **EM2+AP+QS+TF-TuM-13 Structural and Electronic Properties of CdSexTe1-x /CdTe thin-film photovoltaic devices: Carrier Dynamics Analysis by Charge Carrier Collection Efficiency***, **Philip (Sanghyun) Lee**,* University of Kentucky*; Kent Price,* Morehead State University

Polycrystalline Cadmium Telluride (CdTe) thin-film solar cells are among the most successful commercial thin-film solar technologies, achieving a record cell efficiency of nearly 23.1% and offering competitive module costs compared to silicon (Si) modules. More than 20 GW of CdTe modules have been installed worldwide. Laboratory-scale tests have even surpassed 23.1%, getting closer to the theoretical Shockley-Queisser limit of about 32%. Recent research has focused on integrating selenium (Se) into CdTe absorbers to create band grading without the use of CdS window layers. The compound CdSexTe1-x has emerged as a key candidate for enhancing the short-circuit current (Jsc) by lowering the bandgap below 1.45 eV, which could help push short-circuit-current (Jsc) closer to its theoretical limits.

In this study, we fabricated $CdSe_xTe_{1-x}$/CdTe devices with vapor transport technology (VTD) and characterized the structural chemistry and electronic properties of $CdSe_xTe_{1-x}$/CdTe devices from the carrier collection dynamics perspective. The device structure is CdSeTe/CdTe absorbers on TEC-10 glass coated with fluorine-doped tin oxide ($SnO_2$:F), and finished with Gold back metal contact to minimize the impact of unwanted back contact Schottky barrier on carrier dynamics. The devices were treated under $ClCl_2$ ambient at 480 C for grain recrystallization and grain boundary passivation. Selenium (Se) diffuses deeper into the CdTe film to form CdSeTe. The device was then assessed using cross-section using Scanning Transmission Electron Microscopy (STEM) coupled with Energy dispersive X-ray analysis (STEM-EDX) in addition to evaluating device performance and characteristics. The carrier collection is measured by quantum carrier collection efficiency. The results indicate that Se uniformly diffused into CdTe grains, forming CdSeTe, which effectively lowers the bandgap energy to 1.41 eV, which is 40 mV lower than our initial calculation (1.45 eV), which increased photocurrent to 28.66 mA/cm$^2$. The Se concentration is approximately 5-7 %, incorporated into the front interface of $CdSe_xTe_{1-x}$/CdTe films. From the carrier dynamics analysis, the total loss of charge carrier collection is 19.6%, as compared to ideal charge carrier collection at the front heterojunction of $CdSe_xTe_{1-x}$/CdTe. This indicates that there is room to further improve charge carrier collection to achieve higher photocurrent and, thus, efficiency. The UV and violet light charge collection is 5.46 mA/cm$^2$, whereas the red light charge collection is 4.37 mA/cm$^2$. The most charge collection occurs at in-between wavelengths as 18.71 mA/cm$^2$.

11:15am **EM2+AP+QS+TF-TuM-14 Analysis of $KNbo_3$ Crystal Structure Fabricated on $LiNbO_3$ and $LiTaO_3$ Substrate for Piezoelectric Sensors and Devices Applications***, **LAY THITHI**, Asuki Hagiwara, Ryotsuke Arai,* Josai University, Japan

Recently, small scales energy harvester with clean energy sources are in demand for various portable sensors and electronics devices [1]. Piezoelectric materials such as $KNbO_3$ are in focus for new type of sensors and electronic materials due to its high piezoelectric properties, high curie temperature around 450℃ as well as lead free for environmental hazard compared to lead zirconate titanate PZT [2-3]. On the other hand, piezoelectric crystal such as lithium niobate ($LiNbO_3$) and lithium tantalate ($LiTaO_3$) also have been widely used in electronic and communication devices because it has high electro-optical properties as well as high curie temperature which is considered as the most important parameter for device performance [4]. In this study, well-ordered $KNbO_3$film were synthesis on $LiNbO_3$,$LiTaO_3$ single crystals substrate by hydrothermal method aiming for possibility of electro-optical switching devices, energy conversion and other sensing devices.

$KNbO_3$ (100) and (111) structure epitaxially grown on $LiNbO_3$ and $LiTaO_3$ single crystal substrate with various reaction time and conditions. Crystal structure and film thickness were analyzed by SEM and XRD. Grains size ranging from 1-7μm and polycrystalline crystal film with thickness varies 3-10μm were obtained by single reaction. Two different substrates showed different surface morphology and crystal structure to understand lattice matching $KNbO_3$ film synthesis on $LiNbO_3$ and $LiTaO_3$ which is important for piezo electric properties [5].

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11:30am **EM2+AP+QS+TF-TuM-15 Modelling the Surface Electronic Properties of Catalytic Condenser for Programmable Reactions***, **Lars Grabow**, Shengguang Wang,* University of Houston*; Kaida Liu, Ulrick Gaillard,* University of Minnesota*; Rohit Punyapu, Rachel Getman,* Ohio State University*; Matthew Neurock,* University of Minnesota **INVITED**

The evolution of catalyst design has progressed from structural control and optimization to dynamic electronic control of active sites for surface chemistry. This advancement enables precise tuning of active sites via potential, light, or strain applied to material surfaces. Catalytic condensers are novel devices that stabilize charge from an applied potential across a high-κ dielectric film in a thin top layer of carbon with active sites on metal nanoclusters. This talk examines several computational methods to calculate charge condensation on catalytic condensers and the influence on the adsorption of atomic and molecular species.

The tested methods include direct quantum chemical cluster calculations, charged periodic calculations with homogeneous background counter charge, implicit solvation methods, localized countercharge within the vacuum region, and explicit charge transfer atoms within the vacuum region. Density functional theory (DFT) calculations were employed to evaluate these methods, providing insights into the influence of condensed charge on adsorption and assessing the accuracy and computational requirements of each approach.

The study systematically varied the charge on metal surface atoms from -1 to +1 per atom, calculating binding energies for atomic adsorbates such as H, O, N, and C, as well as the molecular adsorbate CO on ideal single crystal 3d, 4d, and 5d transition metal surfaces, namely Cu(111), Ru(0001), and Pt(111). The applicability of each method was explored by examining the range of systems that can be calculated, computational demands, accuracy of results, and potential pitfalls. Cluster calculations, periodic methods, and implicit solvation models were compared, revealing that charged periodic calculations with homogeneous background counter charge and large vacuum region provided the most practical and computationally efficient results. The study also highlights the role of electric fields versus charge, depicting the extent of polarization of adsorbates from charge density difference plots.

Overall, the choice of method remains a tradeoff between accuracy and computational expense. The findings offer general conclusions about catalytic condensers and contribute to the understanding of electronic control in catalytic surfaces, paving the way for future advancements in programmable catalyst design.

## Thin Films
## Room 206 B W - Session TF1+EM-TuM
## Thin Films for Energy III

**Moderator: Feng Yan**, Arizona State University

8:15am **TF1+EM-TuM-2 ALD NASICON/$TiO_2$ Nanocomposite Electrode with Electrochemical Phase Control for High Energy and Power Density Selectivity***, **Daniela R. Fontecha**, Sangbok Lee,* University of Maryland, College Park*; Alexander C. Kozen,* University of Vermont*; Gary W. Rubloff, Keith E. Gregorczyk,* University of Maryland, College Park

Advancements in ionic devices for energy applications (e.g., solid-state micro-batteries and ionic capacitors) require significant development of compatible materials and fabrication processes to enable high performance conduction and storage of ions. Atomic layer deposition (ALD) is uniquely positioned to utilize device fabrication strategies compatible with CMOS-processing due to its high conformality, that enables on-chip deposition of energy storage devices. Development of fast Li-ion conducting ALD films with coinciding electronic conductivity can help push the boundaries of energy and power delivery in microelectronics.

Although amorphous ALD metal phosphates have been well studied as Li-ion conductors for thin film batteries, there is a gap in the materials exploration space with regards to fast-ion-conducting crystalline phases. This work focuses on the Li-Ti-P-O metal phosphate materials system inspired by the fast ion conducting NASICON structure. $LiTi_2(PO_4)_3$ (LTP) has been previously developed as a bulk solid electrolyte with Li-ion conductivities up to $10^{-5}$S/cm. In addition to the fast ionic conductivity achieved by the NASICON crystalline structure, this phase is also capable of accepting additional Li-ions into its structure if there exists an external electron conduction pathway to perform the redox reaction.

In this work, an ALD process for the Li-Ti-P-O materials system is developed into a nanocomposite that contains NASICON LTP grains and anatase $TiO_2$ grains embedded in an amorphous matrix with post-process annealing at 650 °C for 8.5 minutes. The $TiO_2$ provides a source of electron conduction ($2.2 \times 10^{-7}$ S/cm) and the NASICON-type LTP provides a source of fast Li-ion conduction ($9.3 \times 10^{-7}$ S/cm). This ALD nanocomposite electrode was studied electrochemically in a two-electrode beaker cell vs $Li^+/Li$. The NASICON phase is reversible between 1.6 – 3.5 V and the $TiO_2$ anatase grains provide additional Li-ion storage capacity up to 257 mAh/g at 1C and 71% retention at 20 C. When the cell is cycled to 0.5 V vs $Li^+/Li$, the NASICON phase is not reversible but the pseudocapacitance gained from the amorphous matrix increases the stable capacity to 1305 mAh/g at 1C and 61% retention at 20C. These two stable voltage windows show the versatility in applications for microelectronics possible with this ALD materials system that can leverage the high capacity of the amorphous matrix (microbatteries) or the fast kinetics of the NASICON-type phase (pseudocapacitors).

8:30am **TF1+EM-TuM-3 Laser Raster Pattern Control for Uniform Deposition of Hybrid Organic-Inorganic Perovskites via RIR-MAPLE***, **Joshua Ayeni**, Adrienne Stiff-Roberts,* Duke University

Achieving uniform, scalable hybrid organic-inorganic perovskite (HOIP) deposition remains a key challenge, especially for pulsed laser deposition (PLD) systems [1]. Resonant infrared matrix-assisted pulsed laser evaporation (RIR-MAPLE), a variant of PLD, offers gentle deposition of complex, multi-component materials with excellent stoichiometric and structural integrity [2-3]. However, it is difficult to ensure consistent film thickness and spatial uniformity due to a limited understanding of how laser raster patterns (LRP) impact plume dynamics and film growth mechanisms. Despite its crucial role, the impact of LRP on the quality of films deposited by RIR-MAPLE remains underexplored.

This study aims to address these challenges by investigating the impact of LRP on film thickness, spatial uniformity, and optoelectronic properties of $(PEA)_2PbI_4$ thin films, paving the way for scalable industrial applications. $(PEA)_2PbI_4$, a two-dimensional hybrid perovskite known for its exceptional stability and tunable optoelectronic properties, holds promise for applications in light-emitting diodes, solar cells, and photodetectors [4].

Thin films were deposited under high vacuum conditions (~$10^{-5}$ Torr) with five distinct raster patterns (A–E), each varying in mirror positions and rastering speeds to control material distribution. Film thickness and uniformity were measured by profilometry and scanning electron microscopy (SEM), revealing that LRP notably affects deposition outcomes. Patterns A and B produced the thickest films (305-385 nm) with lower radial thickness variations. Markedly, pattern B shows a moderate variation, offering a trade-off between film thickness and spatial uniformity. However, patterns D and E show greater non-uniformity, and C exhibits the largest spatial variation. These results show that variations in LRP greatly affect deposition rates and morphology, highlighting the need for systematic pattern optimization. The study emphasizes the role of plume overlap and local energy dispersion in controlling growth dynamics during deposition.

To enable predictive control over film properties, a simulation-based model is being developed to characterize the behavior of the plume generated under different LRP conditions. Characterizations such as XRD, XPS, PL, UV-Vis, and electrical measurements will be conducted to assess film properties and performance. By relating deposition conditions to intrinsic material properties, this study lays the foundation for scaling RIR-MAPLE to meet industrial demands for hybrid perovskite-based technologies.

This work is supported by the National Science Foundation under Grant No. NSF CMMI-2227551.

8:45am **TF1+EM-TuM-4 Role of Thermodynamics for Low-temperature Processing of Perovskite Chalcogenides: A Combined Approach of Density Functional Theory and Experiment***, **Ramji Velayutham**, Susmita Jana, Kumar Shwetabh, Birabar Ranjit Kumar Nanda, Surendra Anantharaman,* Indian Institute of Technology Madras, India

Semiconductors for optoelectronic devices are an ever growing topic of research for achieving cost-effective, solution-processable, and scalable techniques for applications in energy harvesting and generation. Compared to III-V semiconductors, metal halide perovskites have revolutionized photovoltaic and light emitting technologies as they meet most of the requirements mentioned above. Perovskites with $ABX_3$ structure where A-site can be organic or inorganic(MA, FA, Cs), B-site is inorganic, typically Sn or Pb, and X site can be halides (Cl, Br, I). Bandgap tuning by varying the composition and low-temperature synthesis are advantages of halide perovskites[1,2]. However, the chemical stability and presence of lead are major roadblocks for commercialization of these devices. On the other hand, perovskite chalcogenides with chalcogens provide enhanced stability compared to halide perovskites. The high-temperature phase formation and phase separation in these chalcogenide systems have gained significant attention for developing low-temperature processing of materials[3].Lowering the processing temperatures down to 350 °C has been achieved but not sufficient to develop flexible devices[4].

In this study, we have explored the possibility of synthesizing the perovskite chalcogenides at lower temperature compared to the literature reports. Using density functional theory, we investigate the thermodynamics of phase formation of perovskite chalcogenides, which are dictated by the configuration entropy and chemical potentials. These results are further verified by synthesizing the exact stoichiometric composition using the chemical vapour deposition technique. X-ray diffraction studies to unravel the phase formation at low-temperature will be presented. We will correlate the absorption and emission spectra from the experimental results with the DFT studies. Further, exciton dynamics at low-temperature from the perovskite chalcogenides will be discussed. We believe that our results will pave the way for introducing perovskite chalcogenides in flexible devices.

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2. C. He and X. Liu. Light Sci Appl 12, 15 (2023).

3. C. Wang, R. Nie, Y. Dai, H. Tai, B. Zhu, L. Zhao, Y. Wu, W. Guo, S. Il Seok. Energy Environ. Sci. 17, 1368-1386 (2024).

4. C. Comparotto, P. Ström, O. Donzel-Gargand, T. Kubart, J. J. S. Scragg. ACS Appl. Energy Mater. 5, 6335-6343 (2022).

9:00am **TF1+EM-TuM-5 Alloyed SnO2-Nb2O5 ALD Films for Energy Applications***, Daniel Macayeal, Ian Christiansen, William Rekas, Madison Cooney, Elijah Burlinson, Yubin Han,* ***Alexander Kozen,*** University of Vermont

Perovskite solar cells are a promising alternative to silicon-based solar cells, however their current lifetimes and durability prohibit their commercial viability. One approach is to utilize ALD $SnO_2$ as a dual electron transport layer (ETL) and passivation layer applied using Atomic layer deposition (ALD). ALD is a method ubiquitous in the semiconductor industry for growing thin film materials with atomic scale precision. Sequential alternating pulses of metalorganic and oxidation precursors are delivered to a reaction chamber and react to grow a film on the surface of a substrate. Using the metalorganic precursors TDMA-Sn and $Nb(OEt)_5$, and the oxidation precursors $H_2O$ and $O_3$, we produced and characterized alloyed thin films of $SnO_2$, and $Nb_2O_5$. We will discuss how temperature and oxidation precursor selection impacts growth behavior, optical, and electrical properties of alloyed $SnO_2$-$Nb_2O_5$ thin films, and analyze phase evolution during alloyed film annealing through TTT diagrams. Lastly, we will examine the effect the alloyed $SnO_2$and $Nb_2O_5$ films have on perovskite solar cell performance by evaluating the open circuit potential, quantum efficiency, and degradation behavior.

9:15am **TF1+EM-TuM-6 Femtosecond Laser Ablation (fs-LA) XPS Depth Profiling of Lead Halide Perovskite Thin Film Solar Cells for Space Applications***,* ***Charlie Chandler***[1] *,* University of Surrey, UK*; Dhilan Devadasan, Simon Bacon,* Thermo Fisher Scientific, UK*; Jae Yun,* University of Surrey, UK*; Hongjae Shim,* University of New South Wales, Australia*; Helen Park,* Korea Research Institute of Chemical Technology (KRICT), Republic of Korea*; Tim Nunney,* Thermo Fisher Scientific, UK*; Mark Baker,* University of Surrey, UK

Perovskites are an exciting field of photovoltaic devices which can be used as solar cell materials for space applications. These devices have shown significant improvements over the last decade in both efficiency and stability. The stability of these devices within the deployed environment is a key area of interest. X-ray photoelectron spectroscopy (XPS) depth profiling of different spin-coated formamidinium lead Iodide ($CH_5N_2PbI_3$) based perovskite thin film solar cells, both pristine and following space environmental testing, have been performed. Depth profiling has been carried out using traditional monatomic and gas cluster ion beam (GCIB) bombardment and compared to profiles recorded using femtosecond laser ablation (fs-LA). A femtosecond laser with a 1030 nm peak wavelength and a pulse duration of 160 fs was employed. The monatomic and cluster ion sputtering depth profiles exhibited chemical damage due to preferential sputtering of C, N and I. $Pb^0$ was also observed in the Pb 4f spectrum as a preferential sputtering artefact. fs-LA XPS depth profiles fully retained the true chemical composition of the 500 nm thick perovskite layer [1]. Following different exposures to proton irradiation, fs-LA XPS depth profiling enabled changes in the perovskite chemical composition as a function of depth to be identified and correlated with solar cell performance. An additional propane-1,3-diammonium iodide ($PDAI_2$) surface treatment following perovskite deposition was shown to reduce the extent of ion beam damage due to self-healing.

[1] C.W. Chandler et al., Surface and Interface Analysis 57 (2025) 246–252

9:30am **TF1+EM-TuM-7 Ambient Degradation Mechanism in Halide Perovskite Cs2AgBiCl6 Revealed by ATR-FTIR***,* ***Pulkita Jain***[2]*, Seda Sarp, Eray Aydil,* New York University

Halide perovskites, such as $CsPbX_3$, are promising for optoelectronics but face challenges due to lead toxicity. Among these alternatives, $Cs_2AgBiCl_6$ has gained attention for its favorable optical properties and potential applications in light-emitting devices. In one potential application, $Cs_2AgBiCl_6$ is doped with $YbCl_3$, a well-known luminophore that enables downconversion and quantum cutting—a process where one ultraviolet photon generates two near-infrared photons. In this energy transfer mechanism, the perovskite host absorbs blue photons and transfers the energy to Yb ions, which then relax ($^2F_{5/2}$→$^2F_{7/2}$) and emit near-infrared photons (1.25 eV). In our previous work, we demonstrated that phase-pure $Cs_2AgBiCl_6$ thin films required excess $BiCl_3$ during synthesis to prevent the formation of impurity phases. Using this optimized composition, our Yb-doped films achieved a photoluminescence quantum yield (PLQY) of 50%, attributed to downconversion. However, PLQY decayed to 30% within one week of exposure to ambient conditions. Hypothesizing that this degradation is a surface-related phenomenon, we implemented a surface passivation strategy on both the top and bottom surfaces of the films. This approach resulted in a remarkable increase in PLQY to 75%, which remained stable for over six months.We conducted a time-dependent ATR-FTIR study to investigate further the underlying mechanisms of PLQY decay in non-passivated films. Our findings revealed that water molecules adsorb onto the film surface upon exposure to air, reacting with excess $BiCl_3$ to form BiOCl and HCl. Concurrently, $CO_2$ is adsorbed, forming carbonic acid, which is facilitated by the presence of HCl. We observed an infrared absorption peak at ~1440 $cm^{-1}$ in the FTIR spectrum, attributed to carbonate species, which emerged over time, reinforcing our hypothesis regarding surface reactions. To understand the role of excess $BiCl_3$, we deposited film with a stoichiometric amount of $BiCl_3$ on the ATR crystal and analyzed its FTIR spectrum. The results indicated that while carbonate formed, its intensity was significantly lower and did not change appreciably

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[1] **JVST Highlighted Talk**

[2] **AVS Graduate Research Awardee**

over time. Additionally, we examined passivated films on the ATR crystal, which exhibited similar behavior, suggesting that the observed carbonate formation is due to the presence of $BiCl_3$ and the formation of HCl upon its reaction with water vapor. This finding elucidates why PLQY remains stable in passivated films: the passivant protects the bulk from the ambient gases. These insights into the degradation mechanisms of Yb-doped $Cs_2AgBiCl_6$ thin films highlight the importance of surface passivation in enhancing long-term stability and performance.

9:45am **TF1+EM-TuM-8 High Rate Low Temperature Processing of Cu-chalcopyrite Semiconductors for Solar Cell Applications***, Thomas Lepetit,* Institut des materiaux de Nantes Jean Rouxel, France*; Nicolas Barreau,* Institut des Materiaux de Nantes Jean Rouxel, France*; Sylvain Marsillac, Deewakar Poudel,* Old Dominion University*; Thamer Alaoui, Leo Choubrac, Ludovic Arzel,* Universite de Nantes, France*; Fabien Pineau,* CNRS Photovoltaics, France*; **Angus Rockett**,* Colorado School of Mines, US

This talk describes a method to recrystallize Cu-chalcopyrite semiconductors during processing resulting in a greatly accelerated deposition process while retaining high material quality. While a number of flux materials were tested, AgBr was found to produce rapid recrystallization and greatly improved material properties in finished solar cells. Maximum process temperatures for $Cu(In,Ga)Se_2$ below 450°C with up to a 4x increase in deposition rate were demonstrated. Recent results have extended this work to ultrathin absorber (480 nm) deposited on transparent indium tin oxide back contacts. Related semi-transparent devices have achieved ~12% efficiency, providing the best device performances obtained to date for such thickness.

## Thin Films
## Room 206 B W - Session TF2-TuM
## VSHOP I - Porous Framework Materials & Membranes

**Moderators: Siamak Nejati**, University of Nebraska-Lincoln, **Junjie Zhao**, Zhejiang University

11:00am **TF2-TuM-13 Synthesis of Electrically Conductive Metal-Organic Framework Thin Films***, **Sarah Park**,* Pohang University of Science and Technology (POSTECH), Republic of Korea **INVITED**

Conducting metal−organic frameworks (MOFs) present a compelling prospect for the development of high-performance electronic devices, ranging from electrocatalysts and chemiresistive sensors to supercapacitors. Although MOFs typically exhibit low electrical conductivity due to flat bands determined by highly localized organic states and weak hybridization with inorganic units, significant advances have been made in engineering their electrical properties. Specifically, through precise control of symmetry and energy overlap, highly ordered infinite charge transport pathways in conducting MOF platforms have been established. Nevertheless, for practical device integration, a critical challenge lies in processing these materials into functional thin films. This presentation introduces two distinct approaches for synthesizing conductive two-dimensional MOF thin films: a single-step, all-vapor-phase chemical vapor deposition process, and a solution-processable synthetic approach.

11:30am **TF2-TuM-15 Selective Breathing Behavior in Thin Films of Microporous Coordination Polymers***, **Greg Szulczewski**, Hallie Matherne,* The University of Alabama

Thin films in a family of pillared, microporous coordination polymers with the general formula $M_2(BDC)_2DABCO$, where M is $Ni^{2+}$, $Cu^{2+}$ and $Zn^{2+}$, BDC is benzendicarboxylic acid and DABCO is 1,4-diazabicyclo[2.2.2]octane, were made by a hot vapor synthesis technique. The thin films were characterized by x-ray diffraction, vibrational spectroscopy and scanning electron microscopy. The films were activated by heating under high vacuum and adsorption/desorption isotherms were measured for several volatile organic alcohols. The shape of the isotherms strongly depend on the metal ion of the coordination polymer and the alcohol. In thin films of $Ni_2(BDC)_2DABCO$, methanol adsorption isotherms exhibit a characteristic S-shape that is attributed to lattice expansion or breathing above a critical pressure. Upon removal of methanol from the thin film, the lattice relaxes back to the original structure. The breathing phenomena is attributed to the formation of a network of hydrogen bonds between the methanol molecules and BDC ligand.

11:45am **TF2-TuM-16 Atomic Layer Deposition for Pore Engineering in Covalent Organic Framework Thin Films for Enhanced Membrane Gas Separation***, Zhiwen Chen, **Junjie Zhao**,* Zhejiang University, China

Covalent organic frameworks (COFs) are crystalline networks with ordered pores, large surface area and versatile topologies. Developing pore engineering strategies to fine tune the internal functionality and dimension of COF pores could offer proper pore size and affinity towards small gas molecules, which is crucial for applying COFs to membrane gas separation. Here, we report a pore engineering approach for COFs using atomic layer deposition (ALD). We prepared thin films of an imine-based COF (TPB-DHTA) on porous alumina supports via interfacial synthesis. We found that the amount of ZnO deposited into the COF pores can be precisely controlled by varying ALD cycles. Consequently, the original pore size (1.4 nm) was reduced to 1.05 nm, 0.85 nm, and even below 0.6 nm, leading to an improved the diffusion selectivity of $H_2/CO_2$ through the COF membranes from 93.9 to 278.6 after ALD modification. Moreover, the Zn-O moieties grown into the COF pores were found to shield the $CO_2$-philic ketoenamine groups, which substantially reduced the $CO_2$ solubility in the COF membrane by 262%. Accordingly, the simultaneously increased diffusion selectivity and sorption selectivity for $H_2/CO_2$ led to a 430% improvement of permselectivity for membrane separation, demonstrating the efficacy of our strategy for pore engineering in COFs.

12:00pm **TF2-TuM-17 Synthesizing Hydrophilic Membranes for PFAS Removal via Molecular Layer Deposition***, **Joelle V. Scott**, Mathangi Venkatesh, Jocelyne Booth, David S. Bergsman,* University of Washington

As the global water crisis continues to worsen, the increased need for access to clean water drives the need for better water treatment technologies, such as through the removal of per- and polyfluoroalkyl substances (PFAS). PFAS are a group of toxic compounds that do not biodegrade due to their strong carbon-fluorine backbone. Common PFAS removal methods include absorption and ion exchange resins, but these require expensive and energy-intensive regeneration steps. A more efficient removal technology is membrane separation, which has been shown to be effective at removing PFAS from water. Short-chain PFAS are harder to remove than long-chain PFAS due to their decreased size and increased reliance on end group interactions. Due to the reduced hydrophobicity of PFAS as their carbon chain length decreases, increasing the hydrophilicity of the membrane selective layer may increase the rejection of both long- and short-chain PFAS by reducing hydrophobic interactions between the membrane and the PFAS compounds. However, interfacial polymerization, a traditional membrane synthetic approach, relies on identifying two monomers that can be dissolved in different solvents that are immiscible. The thickness of the resulting membrane also cannot be independently controlled, as it is defined by the monomer diffusion length into the counter solvent. In this work, we use molecular layer deposition (MLD) to synthesize thin film composite membranes with the aim to vary hydrophilicity. This approach avoids the issue of identifying appropriate solvents, allowing for a wider range of selective layer chemistries as well as independent control over film thickness. To demonstrate the effectiveness of this technique for controlling membrane properties, polymers based on polyurea, polyamide, and polyester were explored, measuring hydrophilicity and ability to remove long- and short-chain PFAS. Film composition is confirmed using FTIR and XPS. These are correlated with pure water permeability, salt rejection, and PFAS rejection to determine the impact of monomer chemistry.

## Electronic Materials and Photonics
## Room 207 A W - Session EM1+CPS+MS+PS+SM+TF-TuA

### Advances in Materials and Processes for Devices and Interconnects (FEOL and BEOL)

**Moderators: Moon Kim**, University of Texas at Dallas, **Philip Lee**, University of Kentucky

2:15pm **EM1+CPS+MS+PS+SM+TF-TuA-1 Carborane-Based Blocking Layers and Plasma Removal Strategies for Area Selective Deposition in Semiconductor Patterning***, **Raja Sekhar Bale,*** University of Missouri-Kansas City*; Rupak Thapa,* University of Missouri-Kansas City*; Vamseedhara Vemuri, Nicholas Strandwitz,* Lehigh University*; Anthony Caruso, Michelle Paquette,* University of Missouri-Kansas City

Advancing semiconductor scaling to the 2 nm and angstrom-level nodes requires patterning methods that move beyond the resolution, alignment, and cost limits of conventional top-down approaches. Area-selective deposition (ASD) provides a complementary bottom-up strategy, enabling growth only where desired to reduce process steps, minimize defects, and/or improve integration in back-end-of-line (BEOL) fabrication. This work investigates the use of carborane self-assembled monolayers (SAMs) as blocking layers for ASD. Carborane SAMs are thermally stable, mechanically robust, and chemically tunable, making them strong candidates for selective surface modification in semiconductor patterning. Their role is to define surfaces where deposition should be inhibited, while remaining compatible with BEOL conditions. To explore their processing compatibility, the blocking ability of carborane SAMs toward ALD dielectric oxides was studied alongside plasma-based removal. Using $CF_4/O_2$ and $C_4F_8/O_2/Ar$ chemistries, we carried out blanket plasma etching of carborane SAMs. This presentation will highlight results on carborane SAM formation, blocking behavior, and plasma response, demonstrating their potential as scalable materials for atomic-scale patterning in next-generation semiconductor manufacturing and their compatibility with advanced BEOL integration.

2:30pm **EM1+CPS+MS+PS+SM+TF-TuA-2 Ferroelectricity in Atomic Layer Deposited Wurtzite Zinc Magnesium Oxide Zn1–xMgxO***, **Benjamin Aronson,*** University of Virginia*; Kyle Kelley,* Oak Ridge National Laboratory*; Ece Gunay,* Carnegie Mellon University*; Ian Mercer,* Penn State University*; Bogdan Dryzhakov,* Oak Ridge National Laboratory*; Susan Trolier-McKinstry, Jon-Paul Maria,* Penn State University*; Elizabeth Dickey,* Carnegie Mellon University*; Jon Ihlefeld,* University of Virginia

Ferroelectric wurtzites have garnered interest in the scientific community since first reported in 2019. $Zn_{1-x}Mg_xO$ has shown promise due its low coercive field (2–3 MV/cm) relative to other wurtzites, integrability on flexible polymer substrates, and complementary metal–oxide–semiconductor (CMOS) and back–end–of–line (BEOL)compatible deposition temperatures as low as room temperature. However, the majority of ferroelectric wurtzite thin films – including $Zn_{1-x}Mg_xO$ – have been fabricated using physical vapor deposition (PVD) techniques, which features largely directional growth. Due to the use of high aspect ratio structures in non–volatile memory devices, the ability to conformally deposit ferroelectric wurtzites will contribute to BEOL integration. Atomic layer deposition (ALD) presents an opportunity to overcome this outstanding challenge due to its sequential, self–limiting growth. In this work, $Zn_{1-x}Mg_xO$ thin films with compositions between $x = 0$ and $x = 0.58$ were grown on platinized silicon substrates using plasma–enhanced atomic layer deposition. Films were characterized using X–ray diffraction (XRD), transmission electron microscopy (TEM), and piezoresponse force microscopy (PFM). All films deposited featured a singular out–of–plane *c*–axis textured wurtzite structure. The *c/a* ratio decrease with increasing Mg content indicates the increasing structural distortion. Film structure and structural distortions were further reinforced and visualized via TEM. PFM amplitude and phase hysteresis loops demonstrated polarization reversal in the $x = 0.46$ and $x = 0.58$ films. Ultimately, this finding presents opportunities to further mature the $Zn_{1-x}Mg_xO$ processing space in which ferroelectric switching is possible, as well as explore ALD of other ferroelectric wurtzites.

2:45pm **EM1+CPS+MS+PS+SM+TF-TuA-3 Harnessing Nitrogen-Rich Interfaces in AlN Ferroelectrics***, **Ian Mercer**[1], Erdem Ozdemir, Chloe Skidmore, Benjamin Debastiani, Kazuki Okamoto,* Penn State University*; Sebastian Calderon, Elizabeth Dickey,* Carnegie Mellon University*; Susan Trolier-McKinstry, Jon-Paul Maria,* Penn State University

The importance of interface preparation in the nitride semiconductor and thin film community has long been recognized as critical in controlling nucleation and properties. These AlN ferroelectrics are an enticing pathway toward integrated energy-efficient robust non-volatile memory, displaying CMOS chemical compatibility, large polarizations, and BEOL processing. Although this has not been fully realized in the relatively recent nitride wurtzite ferroelectric community, current convention stems from strictly polar systems like GaN and AlN. However, there is a clear opportunity in engineering electrode interfaces in these systems to aid in film nucleation, reduced leakage, and extended fatigue lifetimes. In this work, we discuss the influence of surface nitriding on a variety of relevant substrates prior to film deposition to enhance film texture and electrical properties. Adding the surface nitriding leads to a discussion on whether nitrogen-rich interfaces can compensate for nitrogen vacancies that migrate to electrode interfaces during cycling. By depositing top and bottom metal nitride electrodes, we investigate the benefits in the electrical properties versus metallic electrodes. Reactive RF magnetron sputtering is employed to co-sputter AlN ferroelectrics. X-ray diffraction (XRD) is used to display *c*-axis texture, while hysteresis (PE), leakage (PUND), and fatigue measurements are used to characterize the electrical properties. Etching/SEM is also used to display partial switching, exploiting the n-polar fast etch in KOH solutions, which helps visualize the effects of nitrogen-rich interfaces. Furthermore, this study reinforces the functionality of interface engineering in AlN ferroelectrics at both the top and bottom electrode interfaces. The importance of this work is that all films in this class may benefit from nitrogen-rich interfaces.

3:00pm **EM1+CPS+MS+PS+SM+TF-TuA-4 Selective Etching of GaN Over AlGaN and Monitoring via Optical Emission Spectroscopy***, **Michael Thomas**, Patrick Wellenius, Spyridon Pavlidis,* North Carolina State University

Achieving etch selectivity between GaN and AlGaN is critical for the repeatable fabrication of enhancement-mode AlGaN/GaN High Electron Mobility Transistors (HEMTs). The selectivity can be tuned by varying the $O_2$ content in a $Cl_2$-based etch. In this work, we explore the etch process parameter space that affects selectivity and explore how *in-situ*optical emission spectroscopy (OES) can be used as an indicator of chamber and plasma conditions over time.

Two epitaxial structures on sapphire were used. The first is a thin film of GaN (control). The second is a device-relevant AlGaN/GaN heterojunction with a GaN cap layer**.** Following photolithography,samples of each type were etched simultaneously in an Oxford Instruments Plasmapro 100 Cobra inductively coupled plasma (ICP) to eliminate run-to-run variation from the selectivity determination. The total etch time was varied by gas composition to keep the HEMT sample etch depth within the AlGaN front barrier. Etch step heights were measured via atomic force microscopy (AFM) in an Oxford Instruments Asylum Research MFP-3D Origin AFM. Using an OceanOptics USB4000 Spectrometer, OES signals were collected with 1 s integration every 60 s during chamber cleaning and conditioning, and every 30 s during the final etches for each composition.

During initial experiments, the chamber pressure, ICP power, and table RF power were all kept constant at 15 mTorr, 500 W, and 25 W, respectively. The total gas flow was kept constant at 50 sccm, and $Cl_2$ was further kept constant at 35 sccm. The remaining 15 sccm were split between $O_2$ and Ar, with three tests being done at 0/15, 2/13, and 4/11 sccm of $O_2$/Ar respectively. An initial peak selectivity of 3.45:1 was measured with 2 sccm $O_2$. The OES signalconfirms $O_2$ emission brightness changes as expected with flow rate. To further improve the selectivity, we will report on the etch characteristics across a wider parameter space, including varying the $Cl_2$ content of the plasma, the total gas flow rate, the chamber pressure, ICP power and substrate size. Moreover, we explore how the OES's utility can be leveraged to assess the effectiveness of pre-etch chamber conditioning to improve both selectivity and repeatability. The results of this study are expected to boost the yield and performance of AlGaN/GaN HEMTs.

This technology was primarily supported by the Microelectronics Commons Program, a DoD initiative, under award number N00164-23-9-G059.

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[1] **JVST Highlighted Talk**

## Thin Films

## Room 206 B W - Session TF-TuA

### VSHOP II - Infiltration Synthesis of Hybrid Materials

**Moderators: Jolien Dendooven**, Ghent University, Belgium, **Mark Losego**, Georgia Institute of Technology

2:15pm **TF-TuA-1 Ruthenium Tetroxide as a Versatile and Selective Precursor for Sequential Infiltration Synthesis of Ru and $RuO_2$***, Nithin Poonkottil, Matthias Minjauw, Brent Van Neste,* Ghent University, Belgium*; Eduardo Solano,* ALBA Synchrotron, Spain*; Arbresha Muriqi,* Tyndall National Institute, University College Cork, Ireland*; Matthias Filez,* Ghent University, Belgium*; Michael Nolan,* Tyndall National Institute, University College Cork, Ireland*; Christophe Detavernier,* ***Jolien Dendooven,*** Ghent University, Belgium **INVITED**

This presentation explores the use of ruthenium tetroxide ($RuO_4$) as a powerful and versatile precursor for atomic layer deposition (ALD) and sequential infiltration synthesis (SIS) of Ru-containing materials. Due to its strong oxidizing character, $RuO_4$ exhibits unique surface reactivity compared to conventional metalorganic precursors. It readily reacts with oxidizable surfaces and polymers, while showing negligible interaction with already oxidized materials [1]. This inherent chemical selectivity is particularly advantageous for nanopatterning applications, such as area-selective ALD and selective vapor-phase infiltration.

ALD or SIS of metallic Ru is achieved by alternating $RuO_4$ and $H_2$ at low temperatures, optimally around 100°C, enabling efficient reduction reaction without decomposition of the $RuO_4$ precursor, which occurs above 125°C. Replacing $H_2$ with a milder reducing agent like methanol results in the deposition or infiltration of $RuO_2$ instead of metallic Ru [2]. Furthermore, alternating $RuO_4$ with metalorganic precursors enables growth of ternary ruthenates [3]. For example, a $RuO_4$–trimethylaluminum (TMA) process yields an aluminum ruthenate with a 1:1 Al:Ru ratio.

$RuO_4$ has long been used in liquid-phase staining of (block co)polymers to enhance contrast in electron microscopy. We demonstrate that its selective reactivity is preserved in the vapor phase: $RuO_4$ reacts with polystyrene (PS) but not with poly(methyl methacrylate) (PMMA) [4]. This selectivity enables targeted SIS within PS-b-PMMA templates. Alternating $RuO_4$ and $H_2$ exposures in such templates, followed by plasma removal of the polymer, yields well-defined Ru nanostructures. Similarly, $RuO_2$ nanopatterns are obtained using $RuO_4$/methanol chemistry in the same template.

Mechanistic insights were obtained using in situ FTIR and DFT calculations, revealing that $RuO_4$ preferentially oxidizes the aromatic CH and C=C bonds in PS, while PMMA remains unaffected. Grazing-incidence wide-angle X-ray scattering (GIWAXS) confirmed the formation of crystalline Ru in the infiltrated PS domains. Microscopy and synchrotron-based X-ray analysis further corroborated the morphological fidelity of the Ru and $RuO_2$ nanostructures to the original PS template, as well as the evolution of contrast with increasing SIS cycles.

1. M. M. Minjauw et al. Chem. Mater. 2019, 31, 1491–1499.
2. N. Poonkottil et al. Chem. Mater. 2022, 34, 8946–8958.
3. M. M. Minjauw et al. Dalton Trans., 2022, 51, 10721–10727.
4. N. Poonkottil et al. Chem. Mater. 2022, 34, 10347-10360.

2:45pm **TF-TuA-3 Extrinsic Cation Incorporation in the Magic Size Indium Sulfide Cluster via Vapor Phase Infiltration***,* ***Kihoon Kim****, Taylor Harville, Donghyeon Kang, Nuwanthaka Jayaweera, Karen Mulfort, Jeffrey Elam, Cong Liu, Alex Martinson,* Argonne National Laboratory

The intentional introduction of impurities into a material is essential for controlling the properties of semiconductor materials from the bulk to the nanoscale. Here, we report the extrinsic cation incorporation into molecular-level semiconductor clusters via vapor phase infiltration synthesis. Exposure of magic-size $In_6S_6(CH_3)_6$ clusters to a conventional volatile organometallic precursor, i.e., dimethyl cadmium, induces the substitutional incorporation of Cd, modifying their optical properties. The extent of cation incorporation can be controlled by adjusting the exposure cycle, reaction temperature, and precursor dosage. Unlike conventional cation incorporation processes, this phenomenon is limited to specific organometallic precursors. The underlying reaction mechanisms are further investigated using density functional theory.

3:00pm **TF-TuA-4 Vapor Phase Infiltration of $VOCl_3$ into P3HT: The Interplay of Doping, Dedoping, and Hybridization***,* ***Li Zhang***[1,2]*, Shawn Gregory, Mark Losego,* Georgia Institute of Technology

Vapor phase infiltration (VPI) of metal halide precursors has been shown effective in the doping of conjugated polymers. Previous publications have found that the conductivity follows a predictable pattern with metal halide exposure time: an initial increase followed by an eventual decrease. The conductivity initially increases due to doping that increases the number of charge carriers. The eventual decrease has been attributed to an increase in the number of scattering sites created by the infiltrated metal oxide clusters. Herein, we explore VPI of the conjugated polymer poly(3-hexylthiophene-2,5-diyl) (P3HT) with $VOCl_3$ + $H_2O$ to modify the conductivity and optical absorbances. Conductivity initially increases with $VOCl_3$ exposure time, peaks around 20 mins to 1 h, and eventually begins to decrease. UV-Vis and XPS measurements at varying hold times confirm that the increased conductivity is due to an increase in the number of charge carriers, as expected. However, at extended exposure times of > 1 h, UV-Vis measurements show an increase in the pi-pi* absorbance and decreasing polaronic absorbance, indicating a decrease in the concentration of charge carriers, not just an increase in the concentration of scattering sites. Furthermore, EDX measurements show a plateauing of the vanadium concentration in the films at ~1 h, meaning no further scattering sites should be created. In situ conductivity and in situ UV-Vis spectroscopy measurements during VPI confirm decreasing conductivity and charge carrier concentrations during the $VOCl_3$ exposure step. From these observations, we postulate that as exposure time increases, $VOCl_3$ can no longer diffuse into the bulk of the film, causing the thermal de-doping rate to exceed the VPI doping rate. This hypothesis is depicted in the attached Figure 1, where between $t_2$ and $t_3$ the effects of thermal dedoping take place starting at the bottom of the film. XPS of the films shows relatively constant doping concentration on the surface regardless of exposure time, but through careful experimentation, we have been able to use XPS to observe a decrease in dopant concentration at the film/substrate interface at times > 1 h, consistent with this proposed bulk de-doping mechanism. Additionally, tests including a vacuum hold step inserted after a 1 h $VOCl_3$ exposure show decreasing conductivity with increasing vacuum hold times, showing that thermal dedoping can occur under vacuum and at the operating temperatures used for this specific process. This work shows the importance of thermal de-doping in designing conductivity of VPI doped conjugated polymer films.

3:15pm **TF-TuA-5 Approaches to Elucidate the Chemical Mechanisms of Atomic Layer Infiltration Processes and Final Hybrid Structures***,* ***Mark Losego,*** Georgia Tech

Further advancing the fundamental understanding of atomic layer infiltration (ALI) processes (also known as vapor phase infiltration, VPI, and sequential infiltration synthesis, SIS) is essential to advancing process development, chemical design, material properties, and application spaces. Fundamentals include both the thermodynamics and kinetics of the process as well as the chemical mechanisms of reaction and inorganic cluster development. Over the past few years, our group has focused on elucidating the latter for several systems, and this talk will discuss what we have learned about approaches to take to understand chemical mechanisms of ALI processes and the physicochemical structure of ALI hybrid materials. An interesting case is the dramatic difference in reaction mechanism between trimethylaluminum and titanium tetrachloride with ester groups in, for example, PMMA. While the TMA reacts directly with and consumes the carbonyl to form a M-O bond, $TiCl_4$ attacks the ether oxygen to form its M-O bond, cleaving the alkyl group and leaving the carbonyl unreacted. These differences elucidate approaches to do purely additive or additive and subtractive chemistry during ALI, opening new application spaces. Moreover, it appears that the bound -$TiCl_3$ moiety remains reactive toward the polymer, forming multiple cross-links which reduces the residual hydroxide concentration (making it less hydrophilic) and increases the connectivity of the polymer. To understand the structural development of the inorganic clusters requires clarifying the oxidation state, coordination number, and chemical state, (e.g., fraction of oxide versus hydroxide). This approach usually requires multiple spectroscopies, whose selection may be limited by the spectroscopic activity or absorption edge of the metal center. A set of deductive processes – applying the constraints of charge state and coordination number – can then be used to develop a model structure and test against additional spectroscopic

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[1] **AVS Dorothy M. and Earl S. Hoffman Scholarship Recipient**

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

evidence or to compare with simulated spectra. Often, spectroscopies that provide next-nearest neighbor and beyond information can help to further elucidate and verify these proposed structures.

4:00pm **TF-TuA-8 Functionalization of Polymer Membranes for Water Treatment using Chemical Vapors***, **Jeffrey Elam**, Seth Darling, Anil Mane, Rajesh Pathak, Bratin Sengupta, Rahul Shevate, Vepa Rozyyev,* Argonne National Laboratory **INVITED**

Polymer membranes are used extensively in water purification to filter and remove particulate and molecular contaminants.Ideally, these membranes should exhibit high permeance, selectivity, and fouling resistance, but these attributes are rarely achieved simultaneously.One approach to improve membrane performance is to modify the polymer using reactive chemical vapors to impart the desired physiochemical properties.In this presentation, I will describe recent work at Argonne using atomic layer deposition (ALD), sequential infiltration synthesis (SIS), and vapor-phase grafting to modify polymer membranes used for ultra- and nano-filtration in water treatment.These techniques rely on self-limiting chemical reactions between gaseous precursors and a solid surface to grow material in an atomically controlled fashion. We have used ALD to produce ultrathin and conformal inorganic layers allowing the membrane pore size and pore wall composition to be precisely tuned, SIS for the bulk modification of polymers by creating an organic-inorganic hybrid material, and vapor-phase grafting of small molecules to achieve additional control over the membrane surface properties.We have also developed methods to accelerate the nucleation and growth of metal oxide layers on polymers to create superhydrophilic, anti-fouling surfaces using only a few ALD cycles.Our studies employ a suite of in-situ and in-operando measurements to elucidate the surface chemistry for these processes and extensive ex-situ characterization and testing to understand the effects of chemical vapor treatment on polymers and how they impact membrane performance.

4:30pm **TF-TuA-10 Resolving Surface Effects and Bulk Properties for VPI-Modified Polymers***, **Seancarlos Gonzalez**, Yuri Choe, Joelle Scott, Agni Biswal, Cecilia Osburn, David Bergsman,* University of Washington

When applying vapor phase synthetic techniques to a porous substrate like a polymer, sometimes there is not a clear delineation between vapor phase infiltration (VPI) and atomic layer deposition (ALD). In ALD, while the objective is often to deposit onto a surface, some diffusion into the subsurface layer is expected. In contrast, VPI can also cause the formation of a surface layer in addition to the components infiltrated throughout the bulk substrate. In some cases, such as for materials for membrane separations, this distinction can have a pronounced impact on device performance. However, the potential presence of a surface layer can complicate material characterization by making it unclear which properties are attributable to the bulk versus the surface.

In this work, we highlight the challenges associated with characterizing the differences between surface and bulk growth in VPI, using an example system based on the infiltration of inorganic and organic reactants into acrylonitrile butadiene styrene (ABS) substrates. First, ABS is infiltrated with diethyl zinc (DEZ) and water to form zinc oxide. It is then infiltrated with 2-methylimidazole (2-HmIM), which can react with zinc oxide to form a metal-organic framework (MOF) known as ZIF-8. Select samples were then exposed to water, which can etch away surface ZIF-8, and then compared against non-etched samples. Successful reactant infiltration was confirmed using secondary ion mass spectrometry (SIMS) to measure reactant infiltration depth, along with thermogravimetric analysis (TGA) to measure reactant loading. Substrates were then examined using x-ray diffraction (XRD) to determine ZIF-8 crystallinity and scanning electron microscopy (SEM) to measure surface morphology, with samples compared with and without surface etching. Results suggest that confinement within the polymer matrix may serve to restrict the crystallization of MOF particles, as opposed to surface deposition where crystallization can proceed unhindered. This distinction can be challenging to characterize due to the limitations of many characterization techniques, and suggests that careful consideration must be given to surface phenomenon, even when using bulk modification techniques like VPI.

4:45pm **TF-TuA-11 Fundamental Studies of the Sorption, Diffusion, and Reaction Processes of Direct Vapor Phase Infiltration of Diethylzinc into PMMA for Hybrid Material Synthesis***, **Typher Yom**, Mark Losego,* Georgia Institute of Technology, USA

Vapor phase infiltration (VPI) is a process that is capable of creating hybrid organic-inorganic materials by allowing a precursor to diffuse a vapor phase inorganic material into a polymer matrix. Doing so can evenly distribute the material throughout the matrix due to the self-limiting nature of the precursor's reaction with functional groups on the polymer. Infiltration of ZnO into polymers is of interest because of ZnO's electrical semi-conductivity, UV absorption, piezoelectricity, and photoluminescence. One hybrid material of interest is zinc oxide mixed with polymethyl methacrylate (PMMA), which is created by the infiltration of diethylzinc (DEZ) into PMMA.In most prior studies, the seeding of ZnO infiltration by first infiltrating with aluminum oxide (via trimethylaluminum) was used because the sorption of DEZ appeared to be low.Here, we use quartz crystal microbalance (QCM) to directly study the sorption and diffusion processes of DEZ in PMMA without a seed cycle. Based on these measurements, we find that DEZ does infiltrate into PMMA at elevated temperatures (>100$^o$C). At 100 $^o$C and below, the added mass from 36 hours of DEZ infiltration is about 25% or less than that of the polymer. On the other hand, at 110 $^o$C and higher, the added mass from 36 hours of DEZ infiltration is at or above about 300% of the mass of the polymer. Additionally, the DEZ does stay inside the PMMA even with long purge times, which would normally remove weakly bound species.This talk will present the sorption rates and diffusion rates for DEZ into PMMA over a range of temperatures from 70 °C to 130 °C. This information will be used to further elucidate the mechanisms of this infiltration process and to what extent ZnO-polymer hybrids can be directly synthesized via vapor phase infiltration.

5:00pm **TF-TuA-12 Impact of Vapor Phase Infiltration on the Mechanical and Chemical Properties of Polyethersulfone Membranes***, Yuri Choe, **Alyssa Hicks**,* University of Washington*; David Bergsman,* university of washington

Vapor phase infiltration (VPI), also known as sequential infiltration synthesis (SIS), is an emerging technique for embedding inorganic materials into polymers using vapor-phase reactants, thereby tuning polymer properties. This technique has the potential to be useful in applications like membrane separations, where improved polymer properties, such as resistance to organic solvents, thermal stability, and selectivity, can substantially reduce processing costs. However, the infiltration of inorganic fillers can reduce polymer ductility, which can inhibit their use. Therefore, understanding the impact of VPI on polymer mechanical and chemical stability is critical for the rational design of robust membranes.

In this work, polyethersulfone membranes—often used as support layer—were treated with trimethylaluminum and water to introduce aluminum oxide via VPI. Exposure duration and process cycles were then modulated to control infiltration depth and inorganic loading, respectively, before measuring mechanical properties through burst pressure testing and dynamic mechanical analysis. Results showed that membranes were less resistant to pressure and more brittle when shallower infiltration depths and higher inorganic loadings were used. These trends were found to agree with theoretical models, such as the rule of mixtures and Gibson-Ashby formulations, which predict that the distribution of alumina would mitigate the loss of ductility. Additionally, the chemical stability of VPI-treated membranes in organic solvents and their separation performance were compared against the alumina infiltration depth, suggesting tradeoffs between chemical and mechanical stability in VPI-modified polymer membranes.

## Atomic Scale Processing Mini-Symposium
## Room 206 A W - Session AP+PS+TF-WeM

### Thermal and Plasma-Enhanced Atomic Layer Deposition

**Moderator: Austin Minnich**, California Institute of Technology

8:00am **AP+PS+TF-WeM-1 High-Temperature Thermal ALD of $SiO_2$ Using Chlorosilane and Aminosilane Precursors: A Comparative Study***, **Okhyeon Kim**, Tanzia Chowdhury, Changgyu Kim, Hye-Lee Kim,* Sejong University, Republic of Korea*; Jae-Seok An, Jung Woo Park,* Hansol Chemical Co., Ltd., Republic of Korea*; Won-Jun Lee,* Sejong University, Republic of Korea

As the number of layers in three-dimensional vertical NAND memory devices continues to increase, the conformal deposition of high-quality $SiO_2$ films in high-aspect-ratio (HAR) structures at high temperatures becomes increasingly critical. Atomic layer deposition (ALD) is the ideal technology for this application, offering atomic-level thickness control and excellent conformality. However, most existing studies on $SiO_2$ ALD have focused on low-temperature plasma-enhanced ALD processes, which are inadequate for producing high-quality films in HAR structures. In contrast, high-temperature thermal ALD of $SiO_2$ films remains underexplored. In this work, we investigated high-temperature (>600 $^{o}$C) thermal ALD of $SiO_2$ using chlorosilane and aminosilane as Si precursors and compared the performance of silicon precursors. Density functional theory (DFT) calculations were first performed to evaluate the precursors based on their thermal stability. Next, the maximum ALD temperature was determined experimentally based on self-limiting behavior and confirmed by step coverage analysis in HAR patterns. Film composition and impurity levels were analyzed by X-ray photoelectron spectroscopy and dynamic secondary ion mass spectroscopy. Stoichiometric $SiO_2$ films were deposited using both chlorosilane and aminosilane precursors, but pure ALD processes were possible at higher temperatures with chlorosilane precursors due to their better thermal stability. Chlorosilane precursors also resulted in lower impurity levels in the film due to their simpler molecular structures, which is consistent with the better electrical properties and wet etch resistance observed. This study combines theoretical and experimental results to provide a basis for advancing high-temperature thermal ALD processes of $SiO_2$ and related materials.

8:15am **AP+PS+TF-WeM-2 Catalyzed Molecular Layer Deposition of Methylene-Bridged Silicon Oxycarbide and the Effect of Annealing on Molecular Structure and Electrical Properties***, **Man Hou Vong**, Seoyeon Kim, Michael Dickey, Gregory Parsons,* North Carolina State University

Silicon oxycarbide (SiOC-H) is a low-k dielectric material capable of minimizing parasitic capacitance between interconnects, thereby lowering the signal delay. As feature nodes in integrated circuits continue to shrink, deposition processes that offer precise control over film thickness and conformity are increasingly critical. Molecular layer deposition (MLD), a vapor deposition technique that deposits molecular layers via self-limiting surface reactions driven by sequential reactant exposure, offers a promising route to meet these demands. Previous studies have demonstrated the feasibility of MLD for methylene-bridged ($Si-CH_2-Si$) SiOC-H using bis(trichlorosilyl)methane (BTCSM) as the precursor and water as the oxidant at moderate temperatures (< 100°C). However, the reported growth rate was limited despite the high reactant exposure. We hypothesize that the limited growth arises from the inefficient direct reaction between the Si-Cl on BTCSM and the Si-OH on the substrate surface. Herein, we introduce a catalyst to overcome the growth limitation in SiOC-H MLD using BTCSM and water. The results show that incorporating catalyst in MLD of SiOC-H at 50°C increases the growth rate by more than ten times under identical reactant exposure. Furthermore, upon annealing at temperatures from 250°C to 550°C, the $Si-CH_2-Si$ bridges undergo a transformation into terminal methyl groups ($Si-CH_3$) via reaction with adjacent Si-OH groups. This transformation increases steric hinderance within the film compared to methylene bridges, reducing the film density and ultimately lowering the permittivity of the films. Overall, the findings in this work provide insights into the role of the catalyst in SiOC-H MLD and highlight its potential for enhancing deposition efficiency for scalable manufacturing in advanced microelectronics fabrication.

8:30am **AP+PS+TF-WeM-3 The Effect of Precursor Choice and Process Temperature on the Properties of ALD Films***, **Theodosia Gougousi**, Nimarta Chowdhary,* UMBC

Precursor choice and process temperature play a critical role in determining the properties of thin films deposited by Atomic Layer Deposition (ALD). In this study, we examine the impact of deposition temperature on the properties of ALD metal oxide films grown using amide-based precursors: tetrakis dimethyl amino titanium (TDMAT) and tetrakis dimethyl amino hafnium (TDMAHf) with water as the oxidizer.

We observe distinct differences between the two precursors. For the Ti process, we find a significant influence of temperature on phase formation and nitrogen incorporation into the films. Films deposited at 100°C crystallize in the anatase phase after inert annealing, while those deposited between 150–300°C transition to the rutile phase. At 350°C, films exhibit mixed phases that vary with thickness. Additionally, films deposited at temperatures above 200°C incorporate oxynitride bonding, significantly affecting both their linear and nonlinear optical properties and electrical conductivity. These variations are most pronounced between 200 and 275°C, a temperature range commonly considered within the "ALD window" for this process.

In contrast, for the Hf process, we do not observe any nitrogen incorporation in the films even at 400°C and the optical and electrical properties of the films are consistent across deposition temperatures. Our findings reveal previously unreported reaction pathways that significantly influence the optical and insulating properties of $TiO_2$ ALD films. Furthermore, we highlight significant differences in the behavior of precursors from the same family emphasizing that extrapolating properties from one materials system to another can be misleading.

This study provides significant insights into the temperature-dependent behavior of ALD-grown $TiO_2$ and $HfO_2$ films, highlighting previously unreported reaction pathways. These findings offer valuable guidance for optimizing film properties in optoelectronic applications and underscore the importance of precise precursor selection in ALD processes.

8:45am **AP+PS+TF-WeM-4 Microwave Enhanced Atomic Layer Deposition (MW-ALD) of $HfO_2$***, **Jessica Haglund**, John Conley Jr.,* Oregon State University

Though beneficial for many applications, the low temperatures typical of ALD can result in residual impurities from unreacted precursors. This can lead to degraded electrical, physical, and optical properties. To improve film quality, post deposition annealing (PDA) can be used. However, the high temperatures necessary for PDAs can exceed thermal budgets, especially in back end of line processing. It has been demonstrated that *post-deposition* microwave annealing can improve film quality and result in lower process temperature.[1] An alternate way to improve film quality is energy enhanced ALD (EE-ALD), in which energy is added during the ALD cycles. Previously, in-situ rapid thermal anneal, plasma, and UV treatments have been added to ALD cycles to drive impurities from films during deposition.[2-6] We have recently introduced in-situ microwave enhanced ALD (MW-ALD) using $Al_2O_3$.[8] Here we discuss low temperature MW-ALD of $HfO_2$.

A custom MKS microwave generator and helical antenna were integrated into a Picosun R200. $HfO_2$ was deposited at 150 °C using 100 TEMA-Hf/$N_2$/$H_2O$/$N_2$ ALD cycles of 1/120/0.2/120 sec. A 30 s 400 W microwave (MW) pulse (without plasma generation) was used during either the TEMA-Hf or the $H_2O$ purge. Film thickness and refractive index were analyzed using a mapping Film Sense FS-1 ellipsometer. MW pulses during the $H_2O$ purge had minimal impact on film thickness and refractive index. However, the same MW pulse during the TEMA-Hf purge resulted in a ~50% increase in thickness and an increase in refractive index. This is consistent with our work on MW-ALD of $Al_2O_3$ which found an increase in film quality when the pulse was applied during the TMA pulse as compared to the water pulse.[8] Additional electrical data will be presented as well as results for depositions at 250 °C.

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9:00am **AP+PS+TF-WeM-5 In Situ Studies of Ald Hf0.5Zr0.5O$_2$ by Spectroscopic Ellipsometry and Reflection Absorption Infrared Spectroscopy**, *Stijn van der Heijden, Alex Neefs,* ***Erwin Kessels****, Bart Macco,* Eindhoven University of Technology, Netherlands

Ferroelectric $Hf_{0.5}Zr_{0.5}O_2$ (HZO) is widely recognized as a leading material for next-generation non-volatile memory technologies, offering excellent scalability and seamless integration with CMOS processing. We have developed an atomic layer deposition (ALD) process for HZO using metalorganic precursors—$HfCp(NMe_2)_3$ and $ZrCp(NMe_2)_3$—in combination with ozone as the oxygen source. This process enables controlled deposition with precise Hf:Zr stoichiometry and uniform film growth under optimized conditions.

In situ spectroscopic ellipsometry (SE) on an Oxford Instruments FlexAL was used extensively during process development to monitor film growth in real time and to extract growth-per-cycle data. Additionally, full TiN/HZO/TiN capacitor stacks were fabricated in a single ALD sequence within the same reactor, allowing us to track film evolution throughout the stack formation. This provided detailed insight into the nucleation behavior and the formation of interfacial layers.

To gain a deeper understanding of the surface chemistry, we employed *in situ* reflection absorption infrared spectroscopy (RAIRS) using a home-built reactor. The RAIRS analysis revealed that formate groups, generated during the ozone pulse, act as active surface sites for precursor adsorption in both the $HfCp(NMe_2)_3$ and $ZrCp(NMe_2)_3$ processes.

Finally, we correlate the findings from SE and RAIRS with the electrical performance of the TiN/HZO/TiN capacitors, offering an integrated view of how surface chemistry and film nucleation influence ferroelectric behavior.

9:15am **AP+PS+TF-WeM-6 Thermal Stability of HfO2 by Incorporating Al2O3 in a MIM Capacitor by 200 mm Batch-ALD**, ***Partha Mukhopadhyay***, Tokyo Electron America*; Ivan Fletcher, Zuriel Caribe, Anton deVilliers, Jim Fulford,* Tokyo Electron America, USA

This work investigates the thermal stability of $HfO_2$-$Al_2O_3$ laminated high-k dielectrics deposited by the high-volume batch atomic layer deposition (ALD) method. At higher crystallization temperatures $HfO_2$ converts from amorphous to polycrystalline and induces nonuniformity in film thickness. The incorporation of $Al_2O_3$ into the $HfO_2$ film forms an HfAlO alloy which presents excellent thermal stability compared to pure $HfO_2$ when annealed at 650°C. Cross-sectional TEM, SIMS and XPS profiles demonstrate the interfacial reaction of these ultra-thin layers where the core-level energy states, Hf4f and Al2p peaks showed a shift to higher binding energy from those of pure $HfO_2$ upon $Al_2O_3$ incorporation (Fig. S2). It is mainly because the Al covalence changes the bonding characteristics and $HfO_2$ becomes more ionic, therefore, the dissociation of the alloyed film is effectively suppressed compared to a pure $HfO_2$ film, indicating an enhanced thermal stability of HfAlO. The fabricated MIM capacitor of low Al-content $Hf_{0.69}Al_{0.31}O$ alloy exhibits a higher capacitance density ($C_pD$) of 12.46 fF/μm$^2$, ~29% better than $HfO_2$ and dielectric constant of $\kappa$>22 than $HfO_2$. The present research indicates a small amount of Al (0.31) incorporation in HfO2 extends its quantization temperature due to stabilizing its crystal phase by reducing oxygen vacancies and traps. It remarkably improved electrical characteristics under thermal stress compared to broken-down HfO2 capacitors under annealing (Fig. S3). While a higher Al content $Hf_{0.44}Al_{0.56}O$ alloy shows excellent thermal stability while possessing 68% higher κ than an $Al_2O_3$ capacitor. It also demonstrated the highest breakdown voltage ($E_{BV}$) of 8 MV/cm and low leakage among the samples. After annealing the degradation of $E_{BV}$ of the $HfO_2$ capacitor is nearly 94% while the $HfAl_{0.31}O$ capacitor faces only 19% (Fig S4). These thin multilayer alloys show excellent relative capacitance variation over the voltage with high $C_pD$, κ-value, low leakage of 10 nA/cm$^2$@3MV/cm, suitable for higher thermal budget BEOL, and interposer process integration for various high bandwidth RF and low-cost memory applications with smaller chip area.

9:30am **AP+PS+TF-WeM-7 Highly Crystalline $ZrO_2$ Films under 2 nm by Atomic Layer Modulation**, ***Wonjoong Kim***, Incheon National University, Republic of Korea*; Ngoc Le Trinh,* Incheon National University, Viet Nam*; Bonwook Gu,* incheon National University, Republic of Korea*; Byungha Kwak,* Ajou University, Republic of Korea*; Hyunmi Kim, Hyeongkeun Kim,* Korea Electronics Technology Institute, Republic of Korea*; Youngho Kang,* incheon National University, Republic of Korea*; Il kwon Oh,* ajou University, Republic of Korea*; Han-Bo-Ram Lee,* Incheon National University, Republic of Korea

As the dimensions of silicon-based devices continue to shrink, achieving both high capacitance and low leakage current becomes increasingly challenging. In particular, the corresponding reduction in thin film thickness makes it difficult to preserve critical physical properties, including crystallinity, thermal stability, and electrical performance. In this work, we investigated yttrium-doped zirconium oxide (YZO) thin films fabricated using atomic layer modulation (ALM), a technique based on atomic layer deposition (ALD). In the ALM process, the surface is sequentially exposed to two precursors with an intervening purging step between each exposure, followed by a reaction with a counter-reactant, resulting in the growth of the YZO film within a single atomic layer. The ratio of Y to Zr in the ALM film is determined by the steric hindrance and chemical reactivity of the precursors with the surface. To design and interpret the experimental process, two theoretical approaches—density functional theory (DFT) and Monte Carlo (MC) simulations—were employed to examine the precursor interactions and their impact on film composition. In ALM films, Y atoms are located closer to Zr atoms, leading to the formation of Y–O–Zr bonds in both the lateral and vertical directions within several atomic layers. Consequently, the ALM film requires a lower energy barrier for diffusion to form the YZO crystalline phase, which enhances film density and improves crystallinity. As a result, YZO films deposited via the ALM process exhibit approximately 250 times lower leakage current density compared to the conventional YZO films fabricated using the ALD under a thickness of 2 nm. This key finding highlights that YZO films prepared by ALM achieve both an increased dielectric constant and reduced leakage current density at low thicknesses, demonstrating their potential as promising materials for future silicon device applications.

9:45am **AP+PS+TF-WeM-8 Influence of Molecular Structure on Ruthenium Deposition: An *in Situ* Study Using Simultaneous Spectroscopic Ellipsometry and Quadrupole Mass Spectrometry**, ***Terrick McNealy-James,*** University of Central Florida*; Xin Kang,* University of Florida, Gainesville*; Luis Tomar,* University of Central Florida*; Johnathon Johnson,* University of Florida, Gainesville*; Novia Berriel, Taylor Currie, Titel Jurca,* University of Central Florida*; Lisa McElwee-White,* University of Florida, Gainesville*; Parag Banerjee,* University of Central Florida

Ruthenium (Ru)with its low bulk resistivity and high work function has emerged as a promising metal for future interconnect technology. Numerous Ru complexes with different ligands have been studied to refine chemical vapor deposition (CVD) and atomic layer deposition (ALD) processes and improve film structure, property and performance. These include molecules such as, bis(cyclopentadienyl)ruthenium [$RuCp_2$],tris(2,2,6,6-tetramethyl-3,5-heptanedionato)- ruthenium [Ru(thd)3] and $\eta^4$-2,3-dimethylbutadiene ruthenium tricarbonyl [$Ru(DMBD)(CO)_3$].[1-3]

Here we investigate the ALD process characteristics of Ru thin films from ($\eta^4$-diene)$Ru(CO)_3$ complexes and resulting film properties. Three molecules are chosen i) η4-isopreneruthenium tricarbonyl, ii) ($\eta^4$-1,3-butadiene)ruthenium tricarbonyl and iii) ($\eta^4$-1,3-cyclohexadiene)ruthenium tricarbonyl; with the rationale of studying the effect of changes to the ligand motif on the film growth characteristics and resulting properties. Furthermore, by employing simultaneous *in situ* spectroscopic ellipsometry (SE) and quadrupole mass spectrometry (QMS), we disambiguate the physical growth mechanisms and chemical reactions occurring at the substrate surface. The resulting Ru film properties are analyzed ex situ using x-ray photoelectron spectroscopy (XPS), x-ray diffraction (XRD) and four-point probe resistivity measurements.

Our *in situ* SE measurements show that, in all cases, deposition occurs for temperatures ≥ 160 °C. No self-saturation in growth behavior is observed. This aligns with QMS data which suggests that all Ru complexes undergo spontaneous dissociation reaction on the substrate surface. The water half-reaction plays no relevant role in promoting deposition. XPS and XRD analyses reveal that all films consist of a $Ru/RuO_x$ mixture in line with high film resistivity. These results highlight the limited role of ligands in controlling the ALD / CVD film growth characteristics of diene-$Ru(CO)_3$ complexes with $H_2O$ as a co-reactant.

11:00am **AP+PS+TF-WeM-13 Study on the Thermal Decomposition Behavior of Mo(Co)6 as a Precursor for Mo-ALD**, *Soken Obara, Souga Nagai, Jun Yamaguchi, Noboru Sato, Naoki Tamaoki, Atsuhiro Tsukune,* ***Yukihiro Shimogaki***, The University of Tokyo, Japan

As miniaturization advances in state-of-the-art semiconductor devices, interconnect resistance becomes increasingly problematic. Atomic layer deposition (ALD) of molybdenum (Mo) is gaining attention as a potential next-generation interconnect technology to replace conventional Cu and W. Although Mo precursors such as $MoCl_5$ and $MoO_2Cl_2$ are commonly used, they present significant drawbacks, including the need for high processing temperatures (~600 °C) and the presence of halogens. In this study, we investigated the thermal decomposition and adsorption behavior of

$Mo(CO)_6$, a halogen-free precursor capable of deposition at lower temperatures, to evaluate its suitability for Mo-ALD.

Using an ALD system equipped with a bubbling delivery mechanism, we deposited Mo films on Si substrates with 100 nm thermal oxide at temperatures ranging from 130 to 175 °C, using $Mo(CO)_6$ and $NH_3$ as precursor and reactant, respectively. Figure 1 shows the ALD process sequence and growth-per-cycle (GPC) as a function of temperature, revealing a steep increase in GPC above 150 °C. As shown in Fig. 2, the precursor pulse time dependence at 145 °C deviates from the ideal ALD self-limiting behavior, indicating a CVD-like growth mechanism.

To investigate the thermal decomposition characteristics of $Mo(CO)_6$, film deposition cycles were performed at 175 °C using only $Mo(CO)_6$ and purge gas, without $NH_3$. As shown in Fig. 3, film formation was observed with a 4-second purge, diminished with an 8-second purge, and disappeared completely with a 14-second purge. This suggests that physisorbed species were gradually removed by purge, thereby suppressing film formation. To determine whether chemisorbed species remained on the surface, a subsequent ALD process with $NH_3$ was performed after an 8-second purge. As shown in Fig. 4, Mo film growth was observed in the downstream region, suggesting that chemisorption persisted even after the longer purge duration.

Step coverage results are shown in Fig. 5. Under ALD conditions at 145 °C and 175 °C with a 4-second purge, step coverage was 100% and 91%, respectively. However, under the 175 °C condition with an 8-second purge, the step coverage exceeded 165%, indicating thicker deposition at the bottom. This result is attributed to residual physisorbed species accumulating at the feature bottom, leading to enhanced local film growth. These findings demonstrate that bottom-up filling can be achieved by tuning the purge time of the precursor.

11:15am **AP+PS+TF-WeM-14 Nucleation Enhancement and Growth Modification in Co-ALD via Pd activation***, **Yubin Deng,*** The University of Tokyo, Japan, China*; Souga Nagai, Jun Yamaguchi, Yuhei Otaka, Noboru Sato, Naoki Tamaoki, Atsuhiro Tsukune, Yukihiro Shimogaki,* The University of Tokyo, Japan

With the continued downscaling of ULSI technologies to the 3 nm node, Cu interconnects demand increasingly thinner liner/barrier layers that can ensure reliable performance under aggressive miniaturization. Previous studies have demonstrated that 1-nm-thick Co(W) films exhibit excellent Cu diffusion barrier properties [1]. However, the critical challenge remains achieving ultrathin, continuous films with precise thickness control. In this context, ALD is considered the most promising technique, offering conformal and selective growth suitable for high-aspect-ratio structures. Importantly, fabricating thinner films via ALD requires higher nucleation densities, which can be promoted by Pd activation. The catalytic properties of Pd enhance precursor adsorption and subsequent surface reactions, thereby improving nucleation. In this study, we systematically investigated the impact of Pd activation on the nucleation behavior and morphological evolution of ALD-Co films.

All samples were prepared on Si substrates with a 300-nm-thick thermally grown $SiO_2$ layer and were cleaned using ethanol and APM. Two Pd activation methods were employed. The conventional wet method involved immersion in a colloidal Sn/Pd solution (0.6 mM $PdCl_2$, 30 mM $SnCl_2$, 0.35 M HCl) at 40 °C for 5 min (Fig. 1), followed by a 3 min rinse in 1 M HCl to remove residual Pd and byproducts, and subsequent drying. Alternatively, Pd activation was performed using ALD (Fig. 2) at 200 °C for 400 cycles, employing palladium(II) hexafluoroacetylacetonate ($Pd(hfac)_2$) as the precursor and aqueous formalin (HCHO) as the reducing agent, with $N_2$ as the carrier and purge gas. Following Pd activation, Co films were deposited via ALD at 150 °C for 500 cycles (Fig. 3), using dicobalt hexacarbonyl tert-butylacetylene (CCTBA) and $H_2$ as the precursor and reactant, respectively.

In the wet method, Pd loading was controlled by varying solution concentration and activation time. While in Pd-ALD, it was precisely adjusted by tuning the precursor pulse count per cycle (supply time). As shown in Fig. 4(a), the wet method failed to deposit sufficient Pd on thermal $SiO_2$, even with extended activation (50 min) and highly concentrated solutions (20×). In contrast, Pd-ALD enabled fine control over the Pd amount, as shown in Fig. 4(b). Figure 5 presents the effects of Pd loading on Co nucleation and morphology. Increased Pd loading resulted in smaller and denser Co nuclei (~9 nm, ~$1.1 \times 10^{12}$ cm$^{-2}$) and enhanced Co deposition. To achieve uniform 1 nm-thick Co films, further optimization of the Pd-ALD process is necessary to reach the target nucleation density (~$10^{14}$ cm$^{-2}$).

**References**

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11:30am **AP+PS+TF-WeM-15 Process-Structure-Properties of Atomic Layer Deposited Niobium Nitride and Evolution of Strain with Plasma Chemistry***, Neeraj Nepal, Joseph Prestigiacomo, Maria G Sales, Peter M Litwin, Vikrant J Gokhale, **Virginia D Wheeler,*** Naval Research Laboratory

Niobium nitride (NbN) has exceptional physical, chemical, and electrical properties that can be utilized in a range of applications such as gate metal, superconducting qubits and detectors ($T_c$ ~9-17 K [1]), RF antennas, resonators, and Cu interconnect diffusion barriers. For all these applications, a low temperature growth process with wafer scale uniformity, conformality, and subatomic thickness control is highly desirable. Atomic layer deposition (ALD) provides a path towards integration of NbN at lower temperatures with control over the desired properties. Most reported thin plasma-enhanced ALD (PEALD) NbN films [2-3] to date are either amorphous or polycrystalline. In this talk, we report on highly oriented single phase, PEALD NbN (111) films and discuss the evolution of strain with plasma chemistry.

ALD NbN films were deposited on resistive Si and c-sapphire in a Veeco Fiji Gen2 ALD reactor using (t-butylimido)tris(diethylamido)niobium(V) (TBTDEN) and $N_2/H_2$ plasma precursors. Similar to previous reports [2], TBTDEN required a boost to enable growth. Growth windows and film morphological, structural, and electrical properties were optimized for TBTDEN temperature (80-100°C), TBTDEN boost (1-2s), TBTDEN pulse (1.5-2.0s), plasma pulse (20-30s), $H_2/N_2$ ratio (1.5-12.5), and temperature (150-400 °C). Optimum growth parameters (TBTDEN = 100°C, TBTDEN boost = 1.5s, TBTDEN pulse = 2s, and $H_2/N_2$ = 60/20sccm) yielded an ALD window from 250-300°C with a growth rate (GR) of ~ 0.5A/cy. While GR was almost constant for $N_2 \geq 20$ sccm, room temperature resistivity ($\rho_{RT}$) increased linearly with $N_2$ flow. High-resolution XRD scans show 1st and 2nd order (111) NbN peaks. Lattice constants obtained from XRD show that strain changes from compressive to tensile with increasing $N_2$ flow, in which an $N_2$ flow of 20 sccm provided an almost strain-free film. The compressively strained 12.6 nm thick film at 5 sccm $N_2$ resulted in lower $\rho_{RT}$ (~139μΩcm) and superconducting critical temperature ($T_c$~12.26K). Measured $T_c$ is similar or higher than reported $T_c$ (12.10K) of 15nm thick ALD NbN films [3]. For an optimized 30nm thick film, carbon is below the XPS detection limit, RMS surface roughness is 0.52nm, and rocking curve FWHM is 0.69°, which is narrower than previously reported for 30 nm thick films [3]. $T_c$ on all those films were also measured to establish process-structure-property relationships, and results will be discussed in the context of use in quantum and high temperature contact applications.

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1. Kalal et al., J. of Alloys Compd. 851, 155925 (2021).
2. Sowa et al., J. Vac. Sci. Technol. A 35, 01B143 (2017).
3. Lennon et al., Mater. Quantum Technol. 3, 045401 (2023).

11:45am **AP+PS+TF-WeM-16 Thin Film Property Modification via Electric Field-Modulated Atomic Layer Deposition***, **Jessica Jones**[1], Shi Li, Francisco Lagunas Vargas, Zachary Hood,* Argonne National Laboratory

Thin, conformal film growth via atomic layer deposition (ALD) is broadly used in microelectronics, photovoltaics, and other industries. Enhanced thin film properties are required to advance device performance.Electric fields affect gas phase molecules, and adsorption behavior, but have not been extensively investigated for direction of thin properties.Static electric fields are generated and maintained *in situ* inside an ALD reactor resulting in modification of crystallinity and chemical composition. Thicknesses were determined via spectroscopic ellipsometry, uniformity was investigated by atomic force microscopy, crystallinity by x-ray diffraction and (scanning) transmission electron microscopy (S)TEM, and chemical composition by x-ray photoelectron spectroscopy. These systems are computationally investigated to probe the mechanism by which the ALD processes are enhanced.

**Acknowledgements:** This material is based upon work supported by Laboratory Directed Research and Development (LDRD) funding from Argonne National Laboratory, provided by the Director, Office of Science, of the U.S. Department of Energy under Contract No. DE-AC02-06CH11357. Work performed at the Center for Nanoscale Materials, a U.S. Department of Energy Office of Science User Facility, was supported by the U.S. DOE, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357.

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[1] **JVST Highlighted Talk**

12:00pm **AP+PS+TF-WeM-17 Thin Conductive Cu Films by In-Situ Plasma Post-Reduction of Atomic Layer Deposited CuO***, Maria Sales, Neeraj Nepal, Peter Litwin, David Boris, Scott Walton,* ***Virginia Wheeler,*** Naval Research Laboratory

Interconnect applications in microelectronics has helped spur the need to develop robust and scalable atomic layer deposition (ALD) processes for copper (Cu). For this application space, the unique advantage of ALD is being able to conformally coat via structures with high aspect ratios due to the self-saturating nature and precise thickness control. Reported ALD recipes for pure Cu typically rely on reactions between a metal-organic Cu precursor and either a thermal or plasma reducing reactant. However, these conventional ALD Cu processes have very low growth rates. Like other metal ALD recipes, ALD Cu typically requires thicknesses of at least 20-40 nm to achieve a fully coalesced, conductive film. Thus, limiting these process in applications where ultrathin highly conductive layers are required.

In this work, we report on an alternative way to obtain conductive Cu thin films by combining CuO with a higher growth rate and faster coalescence with an in-situ plasma reduction. Initially, copper (II) oxide, or CuO, is deposited by PEALD at a substrate temperature of 150 °C, using copper(I)-N,N'-di-sec-butylacetamidinate ($[Cu(^{s}Bu\text{-}amd)]_2$) and Ar/$O_2$ plasma as precursors. The growth rate for this CuO recipe is 0.3 Å/cycle, which is higher than what is obtained for pure Cu using the same precursor (0.1 Å/cycle). Grown CuO films have a low concentration of incorporated ligands and a smooth surface morphology. Following a fixed number of CuO ALD cycles, the CuO film is then exposed to in-situ reducing Ar/$H_2$ plasma pulses. To characterize the resulting films, spectroscopic ellipsometry (SE), X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), and contactless sheet resistance measurements were performed.

Various parameters during the Ar/$H_2$ reducing plasma, such as total exposure time, pulse lengths, and number of reducing plasma cycles, were investigated and effect on key properties of the resultant Cu film, such as chemistry, morphology, and resistivity will be discussed. Additionally, we report on utilizing supercycles of CuO ALD and reducing plasma pulses to grow thicker (30 nm) Cu films with low resistivity. To date, our most optimal CuO-then-post-reduction procedure yielded a 30 nm Cu film with a root mean square (RMS) roughness of 3.3-3.5 nm and a resistivity of 3.8 μΩ cm, which is only a factor of 2 greater than for bulk Cu.

## Electronic Materials and Photonics
## Room 207 A W - Session EM1+AP+CA+CPS+MS+TF-WeM

### Advances in Wide Bandgap Materials and Devices

**Moderator: Erin Cleveland**, Laboratory of Physical Sciences

8:00am **EM1+AP+CA+CPS+MS+TF-WeM-1 Progress in Wide and Ultra-Wide Bandgap Semiconductors – Energy Implications***,* ***John Muth,*** North Carolina State University **INVITED**

The progress in developing wide bandgap semiconductors from idea to commercial products over the past 30 years is one of the great successes of interdisciplinary research between materials, science, physics and electrical engineering. Presently, we are experiencing another step change in the performance of semiconductor devices as ultra-wide bandgap materials (Diamond, Aluminum Nitride, Gallium Oxide) overcome fundamental issues like wafer size, the ability to control conductivity with doping in controlled ways and techniques like wafer bonding become more widely used and high voltage device demonstrations are being made. Similarly, SiC and Gallium Nitride wide bandgap devices are leveraging more mature fabrication technologies including deep ion implantation, sophisticated etching techniques, and high k dielectrics to enable non-planar device geometries, that lower the on resistances and provide increased breakdown voltages. The use of emerging alloys like AlScN offer higher performance higher frequency transistors as well as an addition route to integrate ferroelectric materials with CMOS. Innovations in photonic devices should not be left out with microLEDs for displays and chip to chip communications and increased ability to make low loss visible photonic integrated circuits as well as narrow linewidth lasers for quantum. The goal of this presentation will be to put these advances into context comparing the advances in the different materials and their potential for energy savings for a variety of systems including Artificial Intelligence, Data Centers, and computing and systems where size, weight, power efficiency and reliability matter including ships, planes and satellites.

8:30am **EM1+AP+CA+CPS+MS+TF-WeM-3 Limitations and Effects of Heavy Metal Doping in GaN***, J. Pierce Fix,* Montana State University*; Kevin Vallejo,* Idaho National Laboratory*; Nicholas Borys,* Montana State University*;* ***Brelon May***, Idaho National Laboratory

The doping of third-party elements is the backbone of the microelectronics industry, as it allows delicate control of electron/hole concentration, but it can also be used to imbue a host matrix with unique magnetic or optical properties. Wurtzite gallium nitride is a widely studied large bandgap semiconductor. There are reports of doping GaN with numerous elements, with some being extensively employed in commercial applications. However, there are still a few elements which remain completely unexplored. This work investigates the doping limits and effects of select transition metals, lanthanoids, and actinoids in GaN. The structural, electronic, and optical properties of these first-of-a-kind combinations are presented. Embedding single crystal wide bandgap materials with additional functionality will provide building blocks for new multifunctional hybrid systems for novel sensors, quantum science, or meta-multiferroics. Leveraging the non-centrosymmetric piezoelectric host matrix and atomic-level control of dopant species could allow for active tuning of proximity and correlated phenomena, potentially opening the door for applications of actinide elements beyond nuclear fuels.

8:45am **EM1+AP+CA+CPS+MS+TF-WeM-4 Using Raman Spectroscopy to Characterize Stress and Strain in SiC***,* ***Michelle Sestak***, HORIBA

Raman spectroscopy is a useful, non-destructive tool for measuring stress and strain in materials like silicon carbide (SiC). In this study, we use Raman spectroscopy to analyze stress and strain in three types of SiC samples: as-cut, diamond-lapped, and after chemical mechanical polishing (CMP). By examining shifts in the Raman peak positions, we identify differences in residual stress caused by each processing step. The as-cut samples show high stress due to mechanical damage, while diamond-lapped samples show partial stress relief. The CMP-treated samples exhibit the lowest stress levels, indicating effective surface relaxation. These results demonstrate how Raman spectroscopy can be used to monitor and compare the effects of different surface preparation techniques on stress in SiC materials.

9:00am **EM1+AP+CA+CPS+MS+TF-WeM-5 Nanoscale GaN Vacuum Electron Devices***,* ***George Wang****, Keshab Sapkota, Huu Nguyen, Gyorgy Vizkelethy,* Sandia National Laboratories

On-chip vacuum electron devices that operate by cold field emission have the potential to combine advantages of traditional vacuum electron devices (e.g. vacuum tubes), such as robustness in harsh environments and high frequency operation, together with those of modern solid-state devices, such as size and energy efficiency. By shrinking the vacuum or "air" channel to nanoscale dimensions well below the electron mean free path in air, such devices can operate at ambient pressures while maintaining the physical advantages of ballistic vacuum transport. Here, we present lateral gallium nitride (GaN) semiconductor nanogap field emission diodes and transistors that exhibit ultra-low turn-on voltage, high field-emission current, and that operate in air. The fabrication of these nanoscale devices is enabled by a two-step top-down etching approach allowing for the necessary sidewall verticality and surface smoothness. We present experimental and modeling results on the field emission characteristics of these devices at various nanogap sizes and operating pressures. Initial results showing the potential of these devices for radiation-hardened, photodetection and high-temperature applications will be presented. These results provide critical new insights into the behavior of this new class of devices and point to future challenges and opportunities. *Sandia National Laboratories is managed and operated by NTESS under DOE NNSA contract DE-NA0003525*

9:15am **EM1+AP+CA+CPS+MS+TF-WeM-6 Combining CVD of Graphene and SiC for Efficient Layer Transfer***,* ***Daniel Pennachio****, Jenifer Hajzus, Rachael Myers-Ward,* US Naval Research Laboratory

Remote epitaxy (RE) is a thin film growth technique that incorporates a release layer into the material stack, allowing for transfer of the deposited material with minimal defects [1]. Transferred 2D two-dimensional (2D) material, such as graphene, is commonly used for a release layer, but the transfer step can degrade the film and increase process complexity. To avoid this, we examine *in situ* graphitic carbon growth on SiC substrates before subsequent SiC epitaxy in the same chemical vapor deposition (CVD) RE process. RE SiC and subsequent SiC epilayer transfer is desired since isolated SiC membranes are excellent for quantum photonics and SiC substrate reuse can provide significant cost savings. Despite these benefits, the high-temperature hydrogen-containing CVD environment can damage graphene, making RE difficult under standard SiC growth conditions [2].

This study established growth windows for *in situ* graphene via propane-based hot wall CVD. This propane-based graphene growth enables an efficient transition to subsequent SiC deposition using established SiC growth conditions since it shares a similar hydrogen ambient to standard SiC CVD. Growing at 1620 °C in 20 slm $H_2$ with 20 sccm propane flow produced predominantly monolayer (ML) graphene films on on-axis 6H-SiC(0001) substrates with minimal defects found in Raman spectral maps. Films grown on 4° off-axis 4H-SiC(0001) substrates were multilayer (6 ML) graphitic carbon despite experiencing the same conditions as the on-axis substrates. This optimized graphene growth condition was used for subsequent RE attempts to study the effect of SiC precursor dose, C/Si ratio, and growth rate on epilayer crystallinity and graphene barrier damage. SiC crystalline quality appeared correlated to growth rate, with lower growth rates producing smoother films with fewer polytype inclusions. Single-crystalline, polytype-pure SiC epilayers was achieved on 4° off-axis CVD graphene/4H-SiC(0001). Effects of initial SiC growth parameters on the graphitic carbon release layer were explored via cross-sectional transmission electron microscopy (TEM) and attempts at epilayer transfer. Some growth interfaces exhibited non-uniform multilayer graphitic carbon, motivating further study of this growth system to improve boundary uniformity and SiC epilayer quality.

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

[2] Pennachio, D. J., Hajzus, J. R., & Myers-Ward, R. L. JVST B, 43(2). (2025).

9:30am **EM1+AP+CA+CPS+MS+TF-WeM-7 Multiscale Modeling of Self-heating Effects in AlGaN/GaN High Electron Mobility Transistors (HEMT)**, ***Jerry Comanescu,*** National Institute of Standards and Technology*; Albert Davydov,* NIST-Gaithersburg*; Michael Shur,* Theiss Research, Inc.*; Tyler Gervasio, Behrang Hamadani, Michael Lloyd,* NIST-Gaithersburg

AlGaN/GaN based High Electron Mobility Transistors have emerged as state-of-the-art devices in power and RF electronics because of the outstanding electronic properties of the AlGaN/GaN heterostructure. The large breakdown field of GaN (3.3 MV/cm, 11 times higher than silicon) enables HEMT operation in the kV-range while the high mobility of the two-dimensional electron gas at the AlGaN/GaN interface ensures that HEMTs have a very low on-resistance. In addition, the wide bandgap of GaN makes HEMT devices particularly suitable for high-temperature, high-power, and high-current operations. However, unlike silicon-based devices, the performance of current GaN based devices falls significantly shorter than what is expected based on the outstanding properties of GaN material. This gap in performance is even larger when HEMT devices experience self-heating under high-power operation regime, which strongly affects the device lifetime and reliability. Therefore, understanding the high-temperature operation and the self-heating effect is critical for improving the device design. We report on self-heating effect in AlGaN/GaN HEMTs. We interpret our measurement results using a new compact CAD self-heating model. The model is based on the Unified Charge Control Model (UCCM) and is in excellent agreement with the measured data. Our results allow for the identification of the material properties and device parameters primarily responsible for the temperature dependencies of the device characteristics. The measured temperature dependencies also reveal non-ideal effects related to charge trapping, including threshold voltage instability and current-voltage characteristic hysteresis. The model accounts for the temperature distribution inside the HEMT devices (e.g., distribution of temperature along the channel) which are evaluated by a combination of TCAD simulations, heat transfer finite element simulations, and experiments performed on commercial HEMT devices. The developed compact self-heating model augments TCAD simulations for the Device Technology Co-Optimization approach by linking the AlGaN/GaN HEMT performance and design optimization to material and interface properties.

9:45am **EM1+AP+CA+CPS+MS+TF-WeM-8 Atomic Layer Deposition of High-k Oxide Layers on Aluminum Gallium Nitride: Insight from Time-Resolved Synchrotron Studies***, Nishant Patel, Shreemoyee Chakraborty,* Lund University, Sweden*; Byeongchan So,* lund University, Sweden*; Minho Kim, Alexis Papamichail,* Linkoping University, Sweden*; Rosemary Jones,* Max IV Laboratory, Sweden*; Erik Lind, Vanya Darakchieva,* ***Rainer Timm,*** Lund University, Sweden

Gallium nitride (GaN) and aluminum gallium nitride (AlGaN) are the materials of choice for enabling power electronic devices with superior energy efficiency and very high switching frequency. Such devices are based on metal-oxide-semiconductor (MOS) stacks, where downscaling and leakage control require gate insulators with high dielectric constant, so-called high-k oxides, such as $HfO_2$. However, device performance and especially switching frequencies are often limited by the low quality of the (Al)GaN/high-k interface. Atomic layer deposition (ALD) is typically used for the synthesis of ultrathin, conformal high-k layers, where the choice of oxide material, ALD parameters, and pre-ALD cleaning methods strongly influence film and interface quality. Many important details about the physics and chemistry of the interface formation still remain unknown. Furthermore, until now all efforts to explore the high-k oxide film formation are based on *ex situ* approaches, meaning that film deposition and characterization of the resulting interface occur in separate steps.

Here, we will present a first time-resolved investigation of the ALD reactions of $HfO_2$ on (Al)GaN. We have used synchrotron-based ambient-pressure X-ray photoelectron spectroscopy (AP-XPS) and implemented the ALD process in the AP-XPS setup at the MAX IV synchrotron facility. Thus, we succeeded in mapping surface chemistry and electronic properties *in situ* during subsequent ALD half-cycles, which consisted of the deposition of tetrakisdimethylamido-hafnium (TDMA-Hf) and water. We observed a rather inefficient first ALD cycle, compared to other semiconductor ALD reactions, which improved with increasing aluminum content. Thickness and chemical composition of the resulting Hf-oxide film varied significantly if the order of the precursors was changed (TDMA-Hf first or water first). Both observations are against the established ligand-exchange ALD model and highlight the importance of in-depth studies for improving the quality of high-k layers on (Al)GaN.

In addition, we have used XPS to systematically investigate the electronic properties and chemical composition of the interface between different (Al)GaN substrates and $HfO_2$ or $Al_2O_3$ high-k oxide films, for different ALD temperatures, where $Al_2O_3$ layers typically resulted in a more stoichiometric oxide film. The choice of pre-ALD cleaning methods was also found to be of importance, which can enhance ALD efficiency but also result in significant interface contamination. We will discuss how our structural results can be easily implemented to improve device performance.

## Electronic Materials and Photonics
## Room 207 A W - Session EM2+CA+CPS+MS+SE+TF-WeM

### Processing Ultra-Wide Band Gap $Ga_2O_3$

**Moderator: Daniel Pennachio**, Naval Research Laboratory

11:00am **EM2+CA+CPS+MS+SE+TF-WeM-13 $Ga_2O_3$ Polymorphs: Epitaxial Film Growth, Characterization and Contacts***,* ***Lisa Porter****, Jingyu Tang, Kunyao Jiang, Robert Davis, Posen Tseng, Rachel Kurchin,* Carnegie Mellon University*; Luke Lyle,* Penn State Applied Research Labs*; Carlo Schettini Mejia,* Carnegie Mellon University **INVITED**

The last decade has shown a dramatic increase in research on gallium oxide ($Ga_2O_3$) as an ultra-wide bandgap semiconductor for electronics that can operate in extreme conditions, such as high power, high temperature and radiation exposure. This presentation will focus on unique and intriguing characteristics associated with two processes that are necessary to produce $Ga_2O_3$-based devices: the growth of epitaxial films and the formation of ohmic and Schottky contacts. Whereas $\beta$-$Ga_2O_3$ is the thermodynamically stable phase, the other, metastable, phases of $Ga_2O_3$ can be produced as epitaxial films in either mixed-phase or pure-phase form. Our results, along with those in the literature, indicate that the phase content and other film properties strongly depend on the growth method (e.g., MOCVD, HVPE, mist CVD, etc.) and other conditions during film growth, such as precursor chemistry, flow rates, temperature, and substrate material / orientation. Our group has also conducted comprehensive studies of ohmic and Schottky contacts to $\beta$-$Ga_2O_3$. For reasons that are not well understood, only a few metals have been demonstrated as practical ohmic contacts to $Ga_2O_3$. Whereas Ti/Au contacts annealed at 400–500 °C are widely used, Cr/Au contacts annealed in a comparable temperature range also form ohmic contacts to $Ga_2O_3$. Controlled studies of several different elemental-metal Schottky contacts show that their electrical behavior highly depends on the particular $Ga_2O_3$ surface on which they're deposited; observed behavior ranges from Fermi-level pinning on the (-201) surface to near-ideal Schottky-Mott behavior on the (100) surface. Examples of the phenomena outlined above will be summarized and presented using results from high-resolution transmission electron microscopy, x-ray diffraction, and electrical measurements.

11:30am **EM2+CA+CPS+MS+SE+TF-WeM-15 Compensating Interfacial Parasitic Si Channels in β-Ga2O3 Thin Films Via Fe δ-doping***, **Prescott Evans**, Brenton Noesges, Jian Li, Mark Gordon, Daram Ramdin, Shin Mou, Adam Neal, Thaddeus Asel,* Air Force Research Laboratory, USA

β-$Ga_2O_3$ is a promising material for high power applications given an ultra-wide bandgap and predicted high break down field. One challenge with β-$Ga_2O_3$ for lateral device architectures is the presence of undesired Si between epitaxial thin film and substrate which creates a parasitic conduction channel. This channel limits performance and can prevent device modulation. Attempts to remove this interfacial layer using etch methods have proven mostly successful. However, in plasma-assisted oxide molecular beam epitaxy (PAMBE), conventional removal efforts appear unsuccessful. Our results show interfacial Si can reaccumulate at clean β-$Ga_2O_3$ surfaces from various Si sources inside the MBE tool such as the Si doping effusion cell. Hence, careful growth steps must be considered to avoid Si reaccumulating onto clean β-$Ga_2O_3$ surfaces in PAMBE. This work presents an alternative to mitigate the influence of this Si parasitic conduction channel via Fe delta doping at the interface. We demonstrate how a thin Fe layer at the interface can compensate interfacial Si and create an interface without excess free charge. The growth methodology presented involves multiple steps to avoid Fe diffusion from the interface. We first deposit the Fe followed by a low temperature (LT) undoped buffer before depositing an Si doped channel layer at higher deposition temperatures. The LT buffer helps minimize Fe surface riding and diffusion while the increased substrate temperature during the Si doped channel improves surface roughness. Secondary ion mass spectrometry (SIMS) results show Fe only resides at the interface between substrate and LT buffer layer with Fe concentration in the LT buffer and Si doped channel below the noise floor of the instrument. Furthermore, SIMS shows a smooth transition in Si concentration from the LT buffer into the intentionally Si-doped channel region avoiding any spikes between the two layers, indicating high degree of controlled doping localization. Initial capacitance-voltage (C-V) measurements on samples with the Fe compensation show no spike in carrier concentration near the substrate interface indicating Fe is fully compensating interfacial Si. These results demonstrate a potential method to mitigate parasitic Si conduction channels in β-$Ga_2O_3$. However, time-dependent C-V results show there is some capacitance transients when the sample is fully depleted. While Fe seems initially promising other compensating acceptors such as N or Mg need to be explored given this observation of capacitance transients in Fe-doped structures. Overall mitigating this parasitic interface will help improve yield and performance uniformity in fabricated devices.

11:45am **EM2+CA+CPS+MS+SE+TF-WeM-16 Investigating Metal Gate-Driven Interfacial Reactions in ALD-Grown $Al_2O_3$ on β-$Ga_2O_3$***, **Joy Roy**, Adam A. Gruszecki,* The University of Texas at Dallas*; Khushabu S. Agarwal, Paolo La Torraca, Karim Cherkaoui, Paul K. Hurley,* Tyndall National Institute, University College Cork, Ireland*; Chadwin D. Young, Robert M. Wallace,* University of Texas at Dallas

β-$Ga_2O_3$ is a leading candidate semiconductor for next generation power electronics with the potential to outperform GaN and SiC owing to its high breakdown strength paired with low power losses.[1] Integrating a robust gate dielectric and stable oxide interface is critical in leveraging these properties of β-$Ga_2O_3$.[2] However, this cannot be achieved without also considering the gate electrodes' reactivity and their influence on oxide properties. This work explores interfacial reactions—particularly those associated with oxygen scavenging—and the resulting variations in gate oxide performance induced by Ni and Ti gate metals in $Al_2O_3$ on bulk (001) β-$Ga_2O_3$ substrates.

Interface reactions were analyzed via *in situ* X-ray photoelectron spectroscopy (XPS) in an ultrahigh vacuum (UHV) cluster system. β-$Ga_2O_3$ samples were scanned as-loaded, after atomic layer deposition (ALD) of ~2 nm $Al_2O_3$, and a third time following UHV electron beam deposition of Ni or Ti (~1 nm) to assess changes in interface chemistries. Additional chemical states in $Ga_2O_3$ were below the XPS detection limit after oxide and metal deposition. However, an $AlO_x$ (sub stoichiometric) state appeared in Al core levels (2*p* or 2*s*) after introducing Ti. This, along with a $TiO_x$ state in Ti 2*p*, may imply oxygen scavenging from $Al_2O_3$. While both metals reacted with surface organic residues from metal-organic precursors, Ti exhibits more carbide formation at the gate/dielectric interface. Additionally, MOSCAPs were fabricated with ~12 nm $Al_2O_3$ and 10/100 nm of either Ni/Au or Ti/Au as the gate metal for I-V and C-V characterization. Ni/Au devices showed lower frequency dispersion and over two orders of magnitude lower gate leakage in accumulation than Ti/Au samples, consistent with the XPS findings. Dielectric breakdown strength will be further studied to explore electrical stability of the oxides.

In conclusion, a fundamental understanding of gate metals' influence on interface properties is essential for precisely predicting device behavior in power electronics.

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[2] C. V. Prasad, and Y.S. Rim, Mater. Today Phys. **27**, 100777 (2022).

## Thin Films
## Room 206 B W - Session TF1-WeM

## VSHOP III - Initiated Chemical Vapor Deposition

**Moderators: Kwang-Won Park**, Cornell University, **Stefan Schröder**, Kiel University, Germany

8:00am **TF1-WeM-1 Enzyme Microenvironment Engineering via Initiated Chemical Vapor Deposition***, **Yifan Cheng**,* Virginia Tech **INVITED**

Enzymes enable efficient bioprocessing but often lose activity and stability under process-relevant stressors (e.g., low pH, elevated temperature). Complementary to enzyme-centric strategies such as directed evolution, we engineer the microenvironment of immobilized enzymes to shield them from harsh bulk conditions. Using initiated chemical vapor deposition (iCVD)—an all-dry, low-temperature polymerization—we fabricate conformal polycationic films on supports and subsequently immobilize lactase (β-galactosidase). These iCVD films act as proton-buffering layers that modulate the local pH at the enzyme–solution interface, enabling lactose hydrolysis in acid whey. iCVD offers nanoscale control over film thickness and functionality, compatibility with porous substrates (e.g., membranes), and solvent-free processing advantageous for sensitive biomolecules. By tuning cationic composition, we achieve local pH increases of up to 2 units (100-fold reduction in [$H^+$]) and preserve lactase activity under acidic conditions. Immobilization strategy—random versus site-directed—significantly influences the enzyme's kinetic parameters, and we track the evolution of these parameters over multiple use cycles. This microenvironment-engineering approach provides a general route to stabilize diverse biocatalysts without enzyme-specific re-engineering, linking active-site performance to thin-film and interface control.

8:30am **TF1-WeM-3 Engineering Protonation Depth and Charge Density in Polymers for Ph-Responsive Immobilized Lactase Catalysis***, **Huida Duan**, Junxing Chen, Wei Sun, Yifan Cheng,* Virginia Tech

Polycationic polymer coatings with tunable physicochemical properties have emerged as promising platforms for enzyme immobilization in challenging environments such as low pH. However, how polymer thickness and charge density affect local protonation behavior and enzyme activity remains poorly understood. Here, we investigate the effect of polymer thickness and polycationic monomer composition on the protonation behavior and catalytic performance of immobilized β-galactosidase (LacZ). Copolymer films of glycidyl methacrylate (GMA), providing enzyme immobilization sites, and 2-(dimethylamino)ethyl methacrylate (DMAEMA), imparting protonation-dependent positive charges, were synthesized via initiated chemical vapor deposition (iCVD). Their chemical structures were confirmed by Fourier transform infrared spectroscopy (FTIR). Protonation depth was assessed by analyzing the intensity ratios of N–H bending to C=O stretching vibrations after acid treatment, while enzyme activity was evaluated under both neutral (pH 7) and acidic (pH 4) conditions using both random and site-directed immobilization strategies. FTIR results revealed that protonation was limited to a finite depth of ~255nm, with thinner films (<200nm) achieving complete protonation. Enzyme activity at pH 4 was retained only when protonated polycationic layers were present, and plateaued once protonation depth was saturated. Polymers with higher DMAEMA content (65%) outperformed those with lower content (25%), with activity increases up to 83%. Site-directed immobilization consistently preserved higher activity than random conjugation. These findings highlight the critical role of interfacial proton buffering in enabling biocatalysis under acidic conditions and provide design principles for functional polymer-enzyme interfaces in harsh environments.

8:45am **TF1-WeM-4 Recent Advances in the Understanding of Spontaneous Orientation Polarization in Polymer Thin Films Deposited by Initiated Chemical Vapor Deposition (iCVD)***, **Stefan Schröder**, Torge Hartig, Thomas Strunskus, Tayebeh Ameri, Franz Faupel,* Kiel University, Germany

A recent study demonstrated the formation of a spontaneous orientation polarization effect in polymer thin films deposited via initiated chemical vapor deposition (iCVD). It enables the integration of permanent, high-precision electric fields into electronic devices. However, the understanding of the exact mechanism and dependence on the reaction kinetics is still at an early stage. This work reports on new insights on the polarization process based on theoretical and experimental results. The enhanced understanding enables improved control over the resulting surface potential of the polymer films and discovery of new monomers based on electric dipole moment calculations. Furthermore, a few examples of potential applications will be given.

9:00am **TF1-WeM-5 Surface Roughness Control in Vapor-Deposited Nanocoatings for Bio-Adhesion Mitigation***, **Jessie Yu Mao**, Chengqian Huang, Mengfan Zhu,* Oklahoma State University **INVITED**

Superhydrophobic surfaces offer effective resistance against the adhesion of biomolecules like bacteria and proteins. This property holds promise for their application in medical devices, aiming to mitigate complications such as infections and thrombosis. Hierarchical roughness plays a pivotal role in enhancing superhydrophobicity by providing multiple scales of surface features, which collectively contribute to increased water repellency and reduced adhesion of biomolecules. Traditional fabrication of topographical roughness requires specific substrates or solvent-based processing, which could raise concerns regarding biotoxicity. We constructed topographical roughness using an initiated chemical vapor deposition (iCVD) method that is applicable independent of substrate material and geometry. We studied how the processing parameters affect the formed surface topography and the bio-adhesion properties. In addition, surfaces with hierarchical roughness were created by varying the vapor deposition parameters *in situ*. The hierarchically roughened surface demonstrated superhydrophobicity, with more than 80% reduction in the adhered bacteria and a 98.8% decrease in the surface fibrin clotting, as compared with the homogeneously rough surface. This iCVD technique presents a novel avenue for attaining superhydrophobicity on medical devices to reduce device-related adverse events.

9:30am **TF1-WeM-7 Precision Synthesis of Polymeric Materials Using initiated Chemical Vapor Deposition (iCVD) for Cyber Manufacturing***, **Rong Yang**,* Cornell University

initiated Chemical Vapor Deposition (iCVD) is emerging as a powerful technique for the precision synthesis of polymeric materials. New advances in iCVD-based precision polymerization span the synthesis of shaped particles, strategies to suppress side reactions, and achieving emergent properties, all of which are enabled by engineering non-covalent interactions. This talk highlights one example in which engineering monomer absorption into liquid templates enables the integration of artificial intelligence (AI) for the precision manufacturing of polymeric particles with programmable size, shape, and chemistry. We engineer non-covalent interactions between monomers and mesogens to control monomer partition into a liquid crystal (LC) film, thereby enabling LC-templated continuous polymerization. By tuning the relative strengths of non-covalent cohesive force versus elastic force afforded by the LC template, we guide the synthesis pathway along a variety of trajectories that lead to tailored polymer morphology. In addition, the LC templates are self-reporting, which both guide and optically report on the evolution of the morphology of polymeric particles during continuous polymerization. We perform real-time analysis of the optical outputs using AI, enabling on-the-fly feedback and selection of synthesis conditions to achieve targeted polymer morphology. This capability, combined with the automated and scalable CVD technology, points to a new paradigm of cyber manufacturing for polymeric materials.

9:45am **TF1-WeM-8 PFAS-free initiators for iCVD***, **Torge Hartig**, Hannes Nehls, Tim Pogoda, Joschka Paulsen, Julia Piehl, Thomas Strunskus, Franz Faupel,* Kiel University, Germany*; Tayebeh Ameri,* Kiel University, Germany, Iran (Islamic Republic of)*; Stefan Schröder,* Kiel University, Germany

Initiated Chemical Vapor Deposition (iCVD) is an all-dry method for the solvent-free deposition of ultra-thin conformal polymer coatings. In recent years a large library of more than 100 monomers in iCVD has been established representing an extraordinary toolbox while research on initiators has played a smaller role. TBPO (di-tert butyl peroxide) as the standard initiator in iCVD works generally well in all processes. While the deposition rates of TBPO are no problem in academia, faster rates are often required in industrial application. Hence, a focus on new initiators could open the doors to new process kinetics. Previously fluorocarbon initiators have been used for increased deposition rates. With the recent development of possible PFAS bans and fluorocarbon impact on reactor usage, new high-rate initiators are required for the iCVD process. Within this study the impact of the chemical structure of peroxides, including hydroperoxides, is explored, leading to drastically faster deposition rates.

## Thin Films
## Room 206 B W - Session TF2-WeM
### VSHOP IV - Oxidative Chemical Vapor Deposition & Molecular Layer Deposition

**Moderator: David S. Bergsman**, University of Washington

11:00am **TF2-WeM-13 Ozone-Initiated Oxidative Chemical Vapor Deposition of PEDOT Coatings on 2D and 3D Substrates***, **Blake Nuwayhid**[1], Travis Novak, Jeffrey Long, Debra Rolison,* U.S. Naval Research Laboratory

Vapor-phase routes to organic conducting polymers offer many advantages over more commonly studied solution-phase methods. Conductive polymers often require functionalization to be soluble in an appropriate solvent, and techniques such as spin-coating or drop-casting are generally only suitable for relatively flat substrates. Oxidative chemical vapor deposition (oCVD) is an alternative that allows for control of coatings over complex 3D substrates. Poly(3,4-ethylene dioxythiophene) (PEDOT) is the most widely studied oCVD-fabricated polymer, in which all previous reports used undesirable oxidants such as iron chloride ($FeCl_3$), vanadium oxytrichloride ($VOCl_3$), or antimony pentachloride ($SbCl_5$). The $FeCl_3$ is a low-vapor-pressure solid, whereas, $VOCl_3$ and $SbCl_5$ are highly corrosive liquid precursors. These inorganic oxidative initiators necessitate post-deposition treatments to remove inorganic byproducts from the resulting polymer film. We demonstrate a new approach to oCVD PEDOT using $O_3$ as the oxidation source, resulting in a totally dry and cleaner deposition process than that obtained from the aforementioned oxidants. We deposit PEDOT in a custom-built oCVD reactor in a temperature range of 40–100 °C, in which the process shows monomer adsorption–limited behavior with growth rates decreasing from 1.2 nm/min at 40 °C to 0.24 nm/min at 100 °C for a process pressure of 400 mTorr. We further explore the deposition kinetics and chemical composition as a function of temperature, pressure, and $O_3$ concentration. We find that films deposited at <100 °C are not crosslinked, but a gentle thermal annealing at 100 °C in an Ar atmosphere induces polymer crosslinking as determined by spectroscopic ellipsometry. Compositional analysis using XPS and FTIR show that the as-deposited films are over-oxidized, possessing S=O bonds in the thiophene chain. We further characterize the thermoelectric and electrochemical properties of the $O_3$-deposited PEDOT and introduce additives to boost electronic conductivity.

11:15am **TF2-WeM-14 Oxidative Chemical Vapor Deposition of Nanometer-Scale Polyaniline on Si/Cobalt Phthalocyanine (CoPc) Photocathodes for Enhanced Stability and CO/H$_2$ Selectivity during Photoelectrochemical CO$_2$ Reduction***, **Hyuenwoo Yang**, Yuchen Liu, Seoyeon Kim, Hannah Margavio,* North Carolina State University*; Carrie Donley,* University of North Carolina at Chapel Hill*; Hwan Oh,* Brookhaven National Laboratory*; Renato Sampaio,* University of North Carolina at Chapel Hill*; Gregory Parsons,* North Carolina State University

Photoelectrochemical $CO_2$ reduction ($CO_2RR$) to value-added products offers a promising route for carbon utilization, yet photocathode stability and selectivity remain critical challenges. We present a Si/CoPc/Polyaniline (PANI) photocathode, integrating a p-type Si substrate with cobalt phthalocyanine – carbon nanotube (CoPc-CNT) and a ~10 nm oxidative chemical vapor deposition (oCVD) PANI overlayer, achieving exceptional durability and CO selectivity. The oCVD process enables precise PANI thickness control, optimizing stability without sacrificing catalytic access. At -0.4 V vs RHE in $CO_2$-saturated 0.1 M $KHCO_3$ under 1 sun illumination, Si/CoPc/PANI sustains current density for 24 hours, with faradaic efficiency for CO ($FE_{CO}$) exceeding 88%, far surpassing unprotected Si/CoPc's ~20-minute lifespan due to CoPc detachment. Across -0.4 to -0.8 V, Si/CoPc/PANI maintains stability for 3 hours, retaining $FE_{CO}$ at 89% at -0.8 V. Comparative tests reveal thicker PANI layers (20 nm, 45 nm) reduce current density and fail within 24 hours, highlighting 10 nm as optimal.

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[1] **JVST Highlighted Talk**

UV-vis spectropscopty, x-ray photoelectron spectroscopy (XPS), Raman spectroscopy and Fourier transform infrared spectroscopy (FTIR)characterize oCVD PANI overlayer on Si/CoPc photoelectrode. This synergy of oCVD PANI and CoPc yields a robust photocathode, advancing $CO_2RR$ toward practical applications by addressing stability bottlenecks, with implications for scalable, vacuum-deposited protective layers in energy conversion systems.

11:30am **TF2-WeM-15 Temperature Effects in Oxidative Molecular Layer Deposition (oMLD) of Polypyrrole***, **Mahya Mehregan**, Shima Mehregan, Andrew Reinhard, Matthew Maschmann,* University of Missouri-Columbia*; Matthias Young,* University of Missouri, Columbia

Polypyrrole (PPy) is a conjugated polymer with moderate electrical conductivity (~100 S·cm$^{-1}$) and high theoretical charge storage capacity of 411 mAh/g, making it of interest for electrochemical applications including supercapacitors, batteries, and sensors. Using solution-phase synthesis, the maximum charge storage capacity observed for PPy has been limited to ~140 mAh/g. In recent work, the use of oxidative molecular layer deposition (oMLD) to form PPy was found to enhance the charge storage capacity to >300 mAh/g, but the origins of this effect are not fully understood. In this work, we examine how the deposition temperature used for oMLD over the range of 100–150°C influences the PPy growth chemistry, final polymer structure, and electrochemical properties. We employ in situ quartz crystal microbalance (QCM) during oMLD deposition to understand how growth temperature affects the growth mechanism. We also employ ex situ differential scanning calorimetry (DSC), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), and atomic force microscopy (AFM) to validate the insights from QCM, and measure how the deposition temperature influences polymer structure and morphology. We identify that lower deposition temperatures produce higher amounts of surface sorbed $MoCl_5$ during growth, leading to faster film nucleation and higher $MoCl_x$ residue in the final films. We find that deposition below the glass transition temperature introduces microstructure differences, while deposition above the glass transition temperature produces uniform films. We also report high-energy synchrotron X-ray Diffraction (HE-XRD) of PPy formed at 150°C and compare against electrodeposited PPy. Together, these studies establish a deeper understanding of the process/structure/property relationships for PPy formed by oMLD, informing its use for electrochemical applications.

11:45am **TF2-WeM-16 Oxidative Molecular Layer Deposition of Polythiourea for Nitrate Sensing***, **Shima Mehregan**[1], Mahya Mehregan,* university of missouri*; Erick Gutierrez Monje, Matthias Young,* University of Missouri

Low-cost nitrate sensors are critical to enable efficient use of agricultural nutrients and reduce environmental impact from nutrient runoff. In previous work, we established a new strategy to fabricate low-cost nitrate sensors based on differences in ion transport kinetics through ion-selective membranes. However, to be successful, these membrane layers must be formed with highly reproducible thickness and composition, which is not straightforward with wet-chemical polymer synthesis. In this study, we examine the use of polythiourea (PTU) films formed by oxidative molecular layer deposition (oMLD) of thiourea (TU) and molybdenum pentachloride ($MoCl_5$) as nitrate-selective membrane layers. oMLD provides precise control over PTU membrane thickness, composition, and morphology through sequential surface reactions, providing more reproducible sensors and overcoming the limitations of wet chemical membrane synthesis. We employ *in situ* quartz crystal microbalance (QCM) studies during alternating exposures of TU and $MoCl_5$ to understand the oMLD growth mechanism. We characterize the chemical structure of oMLD PTU using Raman Spectroscopy and X-ray Photoelectron Spectroscopy (XPS) and the microstructure using Scanning Electron Microscopy (SEM). We then report the fabrication of PTU-based thin-film nitrate sensors and apply nonequilibrium anion detection to evaluate their sensitivity in the presence of different anions, including chloride, nitrate, and phosphate. We find that PTU membrane layers are highly selective toward nitrate, and improve nitrate selectivity over chloride relative to commercially available electrochemical nitrate sensors, with high reproducibility among devices. This work establishes oMLD PTU as a viable membrane material for low-cost nitrate sensors.

12:00pm **TF2-WeM-17 Polyurea Molecular Layer Deposition Using Low Melting Point Precursors for Use in Biosensor Design***, **Jay Werner**, Seancarlos Gonzalez, David S. Bergsman,* University of Washington

In biosensor design, biomolecules are often chemically bound to the sensor as part of the detection mechanism. As a result, surface functionalization is a critical part of biosensor design to mediate the connection between the analyte and the detector. Silane-based self-assembled monolayers (SAMs) are commonly used for this purpose, however, because of the sub-nanometer thickness of a true monolayer and the propensity of silanes to form unstable multilayer structures, it can be challenging to create and verify a SAM. Molecular layer deposition (MLD) is a promising tool which may be able to take the place of SAMs in some surface functionalization applications where a stable multilayered film would be acceptable. MLD is a vapor phase deposition process that uses a sequence of organic precursors that react via highly energetic reactions in a self-limiting way. These properties allow for the repeatable, stepwise, and conformal deposition of thin films, even in high aspect ratio features. In this work, we present a polyurea MLD chemistry based on low melting point 2,4-toluene diisocyanate (TDIC) and ethylene diamine (ED) to form a polyurea thin film at room temperature. Previous polyurea MLD processes have used high melting point 1,4-phenylene diisocyanate (PDIC) as an aromatic isocyanate precursor, often requiring heat to achieve sufficient vapor pressure. This heat can complicate the deposition process and reduce precursor lifespan. In contrast, TDIC is a liquid at room temperature and is cheaper and more widely available than PDIC. In addition to characterizing this process' growth behavior and composition, we assess the zeta potential, water contact angle, and primary amine availability for crosslinking chemistry. We also assess how these properties are affected by UV-ozone (UVO) etching treatments, which may be used to improve wettability in biosensor design.

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

## 2D Materials
## Room 208 W - Session 2D+EM+NS+QS+SS+TF-WeA

## 2D Materials: Synthesis and Processing

**Moderator: Tiancong Zhu**, Purdue University

2:15pm **2D+EM+NS+QS+SS+TF-WeA-1 Process Discovery for Quantum Materials*, Stephan Hofmann,*** University of Cambridge, UK **INVITED**

Effective heterogeneous integration of low-dimensional nanomaterials in applications ranging from quantum electronics to biomedical devices requires a detailed understanding of different formation and interfacing reactions and the ability to synergize these processes. Process development largely still follows an Edisonian trial-and-error approach, blind and constraint by conventional reactors. This is not only wasteful and frustratingly slow, but hinders scientific breakthroughs in crystal growth and innovation in new deposition technology. This talk will focus on our cross-correlative, high-throughput operando approaches and combinatorial close-space sublimation (CSS) based process design to accelerate process discovery. We show operando spectroscopic imaging ellipsometry and scanning electron microscopy with machine-learning assisted analysis and parameter space exploration for salt-assisted $WS_2$ layer CVD and TMD oxidation phenomena, and howdirect kinetic process data can open data driven approaches to advance the required understanding of underpinning mechanisms.[1] We show that CSS is a highly promising alternative to conventional powder-furnace chemical vapour deposition, offering superior efficiency, precise structural control, scalability, and adaptable process designs. As part of processability and stability assessment, we also explore oxidation kinetics of TMD materials, [2] aided by atomistic modelling using machine-learned force fields.[3]

[1] Yang et al., Chem. Mat. 37, 989 (2025)

[2] Sahota et al., ACS Appl. Nano Mat., asap (2025)

[3] Gsanyi et al., arXiv:2401.00096, 2023

2:45pm **2D+EM+NS+QS+SS+TF-WeA-3 Selective Area Epitaxy of van der Waals Materials*, Ryan Trice*[1]**, *Stephanie Law,* Penn State University

Two-dimensional (2D) van der Waals (vdW) materials are interesting for a variety of applications, ranging from optoelectronics and photocatalysis to energy storage and topological devices. However, vdW materials synthesized using common techniques like chemical or physical vapor deposition often have a high density of growth-related defects, including grain boundaries, twin defects, pyramidal growth, and spiral defects. While pyramidal growth can be minimized through higher growth temperatures, grain boundaries, twin defects, and spiral defects are much harder to overcome. For many applications, especially in electronics and optics, these defects lead to non-radiative recombination, electron scattering, and other undesirable effects. Furthermore, the fabrication of 2D materials into quantum dots (QDs) through bottom-up methods faces problems with precise location placement and polydispersity in the QDs' diameters. This makes the QDs difficult to characterize and is not ideal for most quantum computing and optical setups. Top-down nanofabrication approaches fix this issue but often cause significant damage to the surfaces or edges of the materials. To address these issues, we used molecular beam epitaxy (MBE) combined with selective area epitaxy (SAE) to grow $Bi_2Se_3$ thin films. SAE is a technique in which thin films nucleate and grow in defined areas on a wafer. This is done using a patterned mask where growth conditions are selected such that the film will only nucleate on the substrate.

In this talk, we will describe SAE growth of $Bi_2Se_3$ on Al2O3 (0001) and Si (111) substrates using an atomic layer deposition SiO2 mask. Etching of the SiO2 mask was done with a wet chemical etch, resulting in micron-scale holes of various shapes and sizes. The processed substrates were then loaded into an MBE chamber for the growth of the $Bi_2Se_3$ film. First, we will discuss the effects of different substrate temperatures on the selective growth of the $Bi_2Se_3$ thin films. Second, we will discuss the geometric influence of variously shaped patterns on the crystal quality of the selectively grown films. Third, we will look at the effect and viability of nano-scale patterns for selective growth of vdW materials. Further studies will focus on using different materials for the substrate and mask. This approach could allow us to grow wafer-scale, defect-free 2D vdW QDs at specified areas on the wafer, thereby increasing the scalability and applicability of these materials to real-world challenges.

3:00pm **2D+EM+NS+QS+SS+TF-WeA-4 Precision Synthesis and Conversion of 2D Materials by Pulsed Laser Deposition with in Situ Diagnostics*, Daniel T. Yimam*[2]**, *Sumner B. Harris,* Oak Ridge National Laboratory, USA*; Austin Houston,* University of Tennessee Knoxville*; Ivan Vlassiouk,* Oak Ridge National Laboratory, USA*; Alexander Puretzky,* Oak Ridge National Laboratory*; Gerd Duscher,* University of Tennessee Knoxville*; Kai Xiao,* Oak Ridge National Laboratory, USA*; David B. Geohegan,* University of Tennessee Knoxville

Over the past few decades, 2D monolayers and heterostructures have become central to nanoscience, offering promising applications in electronics, sensing, and future computing. In addition to their exciting functional properties, significant progress has been made in their bottom-up synthesis and subsequent processing. Techniques such as encapsulation, doping, and implantation in atomically thin 2D materials are crucial to transitioning them from fundamental research to scalable, real-world applications, while enabling the emergence of novel properties. However, the ultrathin nature that makes 2D materials attractive also poses substantial challenges for traditional plasma-based processing methods. To fully harness the potential, it is essential to develop reliable processing techniques that offer precise control and reproducibility.

Pulsed laser deposition (PLD) is a promising non-equilibrium method that allows precise control over the kinetic energy (KE) of ablated species. In this work, we investigate plasma plume interactions with 2D materials using *in situ* plasma diagnostics and optical characterization tools. We demonstrate that a deep understanding and control of plasma plume dynamics enables new approaches for 2D material engineering, including the formation of Janus monolayers, metal atom implantation, and encapsulation with minimal damage. Our approach allows for low temperature substitution and implantation of foreign atoms, such as chalcogens and metals, facilitating the selective synthesis of Janus monolayers and alloys. These findings highlight the potential of PLD to drive the practical advancements in 2D materials for microelectronics and quantum information science.

This work was supported by the U.S. DOE, Office of Science, Materials Sciences and Engineering Division and the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.

**Keywords:** Pulsed laser deposition, chalcogenide substitution, 2D materials, implantation, in situ diagnostics.

3:15pm **2D+EM+NS+QS+SS+TF-WeA-5 AVS Peter Mark Memorial Award Talk: Exploiting Thin Film Phase Diagrams for Synthesizing 2D Transition Metal Dichalcogenides*, Nicholas R. Glavin,*** Air Force Research Laboratory **INVITED**

Synthesis of 2D transition metal dichalcogenides for specific applications in electronics, optoelectronic, and advanced coatings remains a critical bottleneck for many industrial applications. In this talk, we will highlight leveraging thin film phase diagrams to rapidly explore the vast parameter space in synthesizing these novel materials. This technique uses laser processing to locally modify regions within the film and coupled with high throughput characterization, rapidly assesses material state and quality for next generation sensors, optical coatings, and low power electronics.

4:15pm **2D+EM+NS+QS+SS+TF-WeA-9 Designer van der Waals Materials for Quantum Optical Emission**, *Shengxi Huang,* ***Wenjing Wu,*** Rice University **INVITED**

Designer van der Waals (vdW) materials offers enormous opportunities to tune material properties for various applications. Isolated, optically-active defects generated in vdW materials could lead to single photon emission. 2D vdW materials as host materials for single photon emission hold various advantages, such as high optical extraction efficiency from the atomically-thin layered materials, and readiness to integrate with on-chip photonic and electronic devices. However, single photon emission from 2D vdW materials typically suffers from low purity and lack of controllability, due to the sensitivity of these atomically-thin materials to external dielectric environments, surface defects and adsorbents, and strains and wrinkles introduced during material processing. This talk introduces our recent efforts to improve the single photon purity and controllability in vdW materials. We developed novel defect structures that can overcome several current issues, and explored their electronic structure and tunability in optical emission. Through a combination of approaches, including strain engineering, heterostacking, employing optical selection rules for excitation and detection, optimization of material synthesis and handling, we were able to achieve high purity (> 98%) for single photons emitted from 2D

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[1] **JVST Highlighted Talk**

[2] **JVST Highlighted Talk**

transition metal dichalcogenides (TMDs) at cryogenic temperature and in hBN at room temperature. This work provides deep insights into the electronic, spin, and valley properties of TMDs and hBN. It also paves the way towards the application of 2D vdW materials for quantum optical applications. The materials engineering approaches developed here can be applied to the optimization of other optical and quantum materials.

4:45pm **2D+EM+NS+QS+SS+TF-WeA-11 Macroscopic Tin Monochalcogenide Van Der Waals Ferroics: Growth, Domain Structures, Curie Temperatures and Lateral Heterostructures***, **Eli Sutter**, Peter Sutter,* University of Nebraska - Lincoln

2D and layered van der Waals crystals present opportunities for creating new families of ferroics with switchable electric polarization, elastic strain, or magnetic order at thicknesses down to the single-layer limit. Synthesis, however, typically leads to small crystals with sizes ranging from below 100 nm (e.g., for SnTe ferroelectrics) to a few µm (e.g., for SnSe ferroelectrics). The limited size and proximity to edges affects the ferroelectric and ferroelastic domain patterns, restricts the experimental methods available to probe emerging properties, and severely limits the ability to fabricate complex device architectures required for accessing functionalities in van der Waals ferroelectrics.

Here, we report the realization of in-plane ferroelectric few-layer crystals of the monochalcogenides tin(II) sulfide and selenide (SnS, SnSe) whose linear dimensions exceed the current state of the art by up to one order of magnitude. Such large crystals allow the investigation of ferroic domain patterns that are unaffected by edges and finite size effects. Analysis of the abundant stripe domains by electron microscopy and nanobeam electron diffraction shows two distinct domain types, twin domains separated by positively charged walls with alternating head-to-head and tail-to-tail polarization as well as not previously observed purely rotational domains connected by neutral domain walls with head-to-tail dipoles. Access to large ultrathin crystals allowed determining the Curie temperatures of few-layer SnSe[1] and SnS van der Waals ferroelectrics.

Finally, we demonstrate the integration of the ultrathin ferroelectric SnSe and SnS into lateral heterostructures.[2] A two-step process produces crystals comprising an SnSe core laterally joined to an SnS edge-band, as confirmed by Raman spectroscopy, electron microscopy imaging, and diffraction. The ability of the lateral interface to direct excited carriers, probed by cathodoluminescence, shows electron transfer over 560 nm diffusion length from the SnS edge-band. The ferroelectric heterostructures adopt two domain configurations, with domains either constrained to the SnSe core or propagating across the entire SnSe-SnS flakes.

The combined results demonstrate industrial scale in-plane ferroelectrics as well as multifunctional van der Waals heterostructures, presenting extraordinary opportunities for manipulating ferroelectric domain patterns and carrier flow**.**

(1) Sutter, E.; Ghimire, P.; Sutter, P. *J Am Chem Soc* **2024**, *146* (46), 31961-31968. DOI: 10.1021/jacs.4c11558.

(2) Sutter, E.; Ghimire, P.; Sutter, P. *ACS Nano* **2024**, *18* (44), 30829-30837. DOI: 10.1021/acsnano.4c11341.

5:00pm **2D+EM+NS+QS+SS+TF-WeA-12 Machine Learning Analysis of Molecular Beam Epitaxy Growth Conditions***, Mingyu Yu, Ryan Trice, Isaiah Moses, Wesley Reinhart, **Stephanie Law**,* Penn State University

Machine learning models hold the potential to explore parameter space autonomously, quickly establish process-performance relationships, and diagnose material synthesis in real time. This reduces reliance on manual intervention in parameter space exploration, enabling more precise and efficient mechanistic control. For molecular beam epitaxy (MBE), despite its breakthroughs in materials synthesis, its stringent growth conditions and complex epitaxial mechanisms make the process of optimizing growth process time-consuming and expensive. Therefore, leveraging machine learning to develop autonomous MBE growth platforms presents a highly promising prospect.Our study on the multi-modal machine learning-guided MBE synthesis is based on a comprehensive high-quality dataset of GaSe thin films grown on GaAs (111)B substrates.GaSe is an emerging two-dimensional semiconductor material with intriguing properties, including thickness-tunable bandgaps, nonlinear optical behaviors, and intrinsic p-type conductivity.Moreover, as a representative member of the van der Waals (vdW) chalcogenide semiconductor family,insights gained from studying GaSe can be extended to other vdW chalcogenides. In this work, we aim to leverage machine learning to analyze the relationships between growth conditions (Ga flux, Se:Ga flux ratio, and substrate temperature) and the resulting sample quality, as well as the correlations among various characterization results including in situ RHEED patterns and ex situ x-ray diffraction rocking curve full-width at half maximum (FWHM) and atomic force microscopy (AFM) root mean square (RMS) roughness. Unsupervised learning on RHEED patterns reveals a well-defined boundary between high- and low-quality samples, capturing physically meaningful features. Mutual information analysis shows a strong correlation between RHEED embeddings and rocking curve FWHM, while the correlation with AFM RMS roughness is weak. Among key growth conditions, growth rate most strongly influences FWHM, whereas the Se:Ga flux ratio primarily affects RMS roughness and the RHEED embeddings. Supervised learning models trained to predict FWHM and RMS roughness demonstrate moderate accuracy, with significant improvement achieved by incorporating RHEED embeddings. Furthermore, anomaly detection via residual analysis in supervised learning aligns well with unsupervised classification from RHEED, reinforcing the reliability of the predictive models. This study establishes a data-driven framework for machine learning-assisted MBE, paving the way for real-time process control and accelerated optimization of thin-film synthesis.

5:15pm **2D+EM+NS+QS+SS+TF-WeA-13 Promoting Crystallographic Alignment in SnSe Thin Films using Step Edges on MgO by MBE***, **Jonathan Chin**, Marshall Frye, Joshua Wahl, Kayla Chuong,* Georgia Institute of Technology*; Mengyi Wang, Derrick Liu,* Pennsylvania State University*; Mingyu Yu,* University of Delaware*; Qihua Zhang, Nadire Nayir, Adri van Duin, Maria Hilse, Stephanie Law,* Pennsylvania State University*; Lauren Garten,* Georgia Institute of Technology

SnSe is a van der Waals material that can be scaled down to two dimensions,[1] making it a promising candidate for nanoelectronics such as field effect transistors (FETs).[2] SnSe in the orthorhombic *Pnma* structure exhibits significant electrical anisotropy where thecarrier mobility is 45% higher along the [010] direction than the [001] direction in plane,[3] making it necessary to control the in-plane alignment of 2D films for integration into electronic devices. SnSe has been shown to form planar coverage on (100) MgO,[4] with which it has a 1.4% and 5.5% lattice mismatch along the [010] and [001] directions, respectively. However, despite the distinct axial lattice matches, in-situ reflective high-energy electron diffraction (RHEED) shows no preferential SnSe film alignment for films deposited on uncleaved MgO. Therefore, to promote orientation control, we cleaved and annealed the MgO substrates to produce step edges along the surface to increase the local surface energy, thereby encouraging atomic adsorption and alignment. SnSe thin films were then deposited from individual Sn and Se effusion cells via molecular beam epitaxy (MBE) onto the prepared MgO substrates heated to 280 °C for 1-5 minutes with a 1.35:1.00 Se:Sn flux ratio at a 0.083 Å/s growth rate to track the nucleation and growth of SnSe grains. The phase of the SnSe films was confirmed by Raman spectroscopy, exhibiting the characteristic $A_g^2$, $B_{3g}$, $A_g^3$, and $A_g^4$ phonon modes.[5] In-situ RHEED confirmed the in-plane alignment along the [010] and [001] by RHEED relative to the [100] substrate, matching theory projections made using reactive force field (ReaxFF) simulations. Additionally, atomic force microscopy (AFM) shows SnSe grains nucleating at step edges on MgO, while scanning transmission electron microscopy (STEM) reveals how the aligned SnSe grains propagate laterally off step edges, maintaining crystallographic alignment throughout the film layer. Overall, our results demonstrate that SnSe grains preferentially nucleate along the step edges produced parallel to the [100] edge of the MgO substrates. The alignment of a 2D vdW film facilitated by step edge formation demonstrates how to achieve orientated depositions of similar anisotropic vdW films on a substrate of choice, ultimately facilitating the manufacture of 2D nanoscale electronic devices.

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5:30pm **2D+EM+NS+QS+SS+TF-WeA-14 Synthesis of Millimeter-Scale Single-Crystal α-$MoO_3$ Nanosheets on Sapphire***, **Ryan Spangler**,* Pennsylvania State University*; Thiago Arnaud, Joshua Caldwell,* Vanderbilt University*; Jon-Paul Maria,* Pennsylvania State University

α-$MoO_3$ is a van der Waals layered semiconductor with biaxial anisotropy that has recently gained interest as an emerging 2D material with a wide band gap (~3 eV), large work function, and high permittivity. Additionally, α-

$MoO_3$ exhibits extreme anisotropy of the dielectric function, enabling in-plane and out-of-plane elliptic or even hyperbolic behavior at various wavelengths. Therefore, α-$MoO_3$ also possesses great potential for nanophotonics through the low-loss and directional propagation of hyperbolic phonon polaritons, which result from the interaction of light with lattice vibrations in highly anisotropic polar materials. However, the lack of single-crystal thin film growth techniques limits further advancement of α-$MoO_3$. In this work, we describe a process for the growth of ultra-large, thin, and atomically smooth single crystals of α-$MoO_3$ directly on *a*-plane sapphire using an alkali-assisted physical vapor transport method. Important parameters necessary for high-quality growth to be discussed include substrate selection, alkali-to-$MoO_3$ ratio, and substrate temperature. The growth proceeds through a vapor-liquid-solid (VLS) mechanism enabled by the formation and liquefaction of low-melting point alkali molybdate phases. This growth mode greatly enhances lateral expansion to several millimeters and thicknesses ranging from hundreds of nm down to <5 nm. This is far thinner and more expansive than crystals grown without alkali metal additives, which can exceed several micrometers in thickness while being limited to a few tens of micrometers in lateral dimensions. The thin alkali-assisted sheets exhibit clean step-flow growth without grain boundaries over mm-scale areas as revealed by atomic force microscopy and polarized optical microscopy. Raman spectroscopy and X-ray diffraction indicate the high crystalline quality of the α-$MoO_3$ films rivaling that of accessible bulk crystals. We will also investigate the propagation of hyperbolic phonon polaritons using scanning near-field optical microscopy (SNOM) to compare hyperbolic phonon polariton lifetimes to values obtained from exfoliated bulk crystals. We find that this growth technique is suitable for exfoliation-free large-scale single-crystal α-$MoO_3$ for nanophotonics and other applications.

5:45pm **2D+EM+NS+QS+SS+TF-WeA-15 Studying the Impacts of Growth Temperature and Seeding Promoters on the Structural and Optoelectronic Properties of $ReS_2$ Grown by CVD***, **Elycia Wright**, Kedar Johnson, Amari Gayle, Robin Rouseau, M.K. Indika Senevirathna, Michael D. Williams,* Clark Atlanta University

Rhenium disulfide ($ReS_2$) is a fascinating member of the transition metal dichalcogenide (TMD) family, which has recently gained significant attention due to its distinct distorted octahedral 1T crystal structure characterized by triclinic symmetry. This distinctive structure shows that $ReS_2$ holds remarkable properties, including anisotropic electronic, optical, and mechanical characteristics. Unlike other TMDs such as $MoS_2$, $MoSe_2$, $WS_2$, and $WSe_2$, $ReS_2$ possesses a band structure that remains consistent regardless of the layer thickness. Due to weak interlayer coupling, it maintains a direct band gap in its bulk and monolayer forms. This unique characteristic makes $ReS_2$ particularly promising for applications in highly responsive photodetectors. To maximize the potential of $ReS_2$ for optoelectronic applications, it is essential to address the challenges associated with its anisotropic growth, distorted structure, and weak interlayer interactions. The anisotropic nature of $ReS_2$ can lead to variations in growth rates in different directions, resulting in multidomain structures that complicate the production of single-crystal $ReS_2$ on a large scale.

In this study, we will synthesize $ReS_2$ by chemical vapor deposition (CVD) at various temperatures and utilize seeding promoters to facilitate the growth of single crystals with continuous layers. We will employ advanced techniques such as confocal microscopy, Raman spectroscopy, and photoluminescence spectroscopy to systematically investigate how the growth temperature and seeding promoters affect the structural and optoelectronic properties of $ReS_2$.

6:00pm **2D+EM+NS+QS+SS+TF-WeA-16 Growth and Characterization of InSe Thin Films on GaAs(111)B and Si(111)***, **Maria Hilse**,* Penn State University

Urgent societal and environmental needs have sparked searches for high-mobility 2D materials with sizeable bandgap and decent stability under ambient conditions for use in ultra-low power, ultra-high performance field effect transistors. With a carrier mobility exceeding 1000 $cm^2/Vs$, small electron effective mass, flat electronic band dispersions, excellent optoelectronic, possible ferroelectric properties and a close-to-ideal solar spectrum matched bulk bandgap of 1.26 eV, InSe shows high potential for future use in electronics. Due to the layered nature, and the many members of different polytypes in the InSe materials family, intriguing confinement phenomena and exotic electron-hole coupling mechanisms tunable by the number of single layers add to the potential wealth of properties in InSe.

In this study, InSe thin films were grown by MBE on GaAs(111)B and Si(111). The presence of many InSe phases required a systematic mapping of the growth parameters to identify conditions for single-phase, single-polytype, and single-crystal growth. Through structural characterization in- and ex-situ using reflection high-energy electron and X-ray diffraction, growth conditions for solely gamma-phase, crystalline InSe films were found. Although the structural properties of the films presented nearly unchanged over a small window of growth conditions, the film morphology was seen to sensitively depend on the Se:In flux ratio. Raman spectroscopy confirmed the phase and polytype assignment deduced from large-area structural characterization.

Microstructure analysis, however, revealed a high degree of structural defects in the films. Nano-scale domains of varying single layer stacking sequences, high-angle rotational domains as well as single layers of unusual bonding configuration resulting in a novel InSe polymorph were found in the films. The total number of defects and the general locations of the new polymorph varied in films across GaAs and Si. The highest structural homogeneity was found for InSe films grown on Si.

Density functional theory calculations for a representative selection of the experimentally observed defects confirmed that most defects, including the novel polymorph have formation energies at or below the thermal budget of the MBE synthesis process. Although the bandgaps of all InSe polytypes and polymorphs possess comparable values, large differences were found in their relative offsets. Due to the random distribution of polytypes and polymorphs in the film, our study suggests a high degree of electronic disorder in these films. Electrical transport showed a variable-range hopping-like behavior supporting the hypothesis of electronic disorder.

## Atomic Scale Processing Mini-Symposium
## Room 206 A W - Session AP+PS+TF-WeA

### Thermal and Plasma enhanced Atomic Layer Etching

**Moderators: Eric Joseph**, IBM T.J. Watson Research Center, **Greg Parsons**, North Carolina State University

2:15pm **AP+PS+TF-WeA-1 Selectivity During Spontaneous Dry Thermal Etching of Si-Based Materials by Hydrogen Fluoride***, Marcel Junige, Micah Duffield, **Steven George**,* University of Colorado at Boulder

Spontaneous dry thermal etching involves reaction of a thin film surface with a gaseous etchant leading to material removal with a constant etch rate. Spontaneous dry thermal etching can often be involved as a competitive process during thermal atomic layer etching (ALE). Selectivity can occur during spontaneous dry thermal etching with hydrogen fluoride (HF) because HF can form different etch species, $F^-$ or $HF_2^-$, that etch with material specificity. For example, $F^-$ can etch $SiN_x$ and $HF_2^-$ can etch $SiO_2$. The nature of the active HF etch species can be controlled by the HF environment. HF alone yields $F^-$ etch species. HF together with a polar co-adsorbate can yield $HF_2^-$ etch species.

The talk will discuss four examples of HF selectivity: $SiN_x$ etch vs $SiO_2$ non-etch; Si etch vs $Si_3N_4$, SiCOH and $SiO_2$ non-etch; Si etch vs Si non-etch with co-adsorbed $H_2O$; and $SiO_2$ non-etch vs $SiO_2$ etch with co-adsorbed $NH_3$ or $(CH_3)_2NH$ (dimethylamine). The experiments were conducted using *in situ* spectroscopic ellipsometry to monitor the film thicknesses during time to obtain etch rates. Additional quadrupole mass spectrometry (QMS) analysis was able to monitor the presence or absence of etch products during the experiments for Si etch vs Si non-etch with co-adsorbed $H_2O$.

Selective $SiN_x$ etch vs $SiO_2$ non-etch was observed for HF etching at 275°C. Etch selectivity was measured for HF pressures from 0.5 to 9.0 Torr. $SiN_x$ : $SiO_2$ etch selectivity approached a maximum of 150 : 1 at 9.0 Torr. These results are consistent with $F^-$ as the active etch species that yields $SiN_x$ etching. Si etch vs $Si_3N_4$, SiCOH and $SiO_2$ non-etch was also demonstrated for HF etching at 275°C and an HF pressure of 3 Torr. Crystalline Si etched at 23 Å/min. In comparison, $Si_3N_4$, SiCOH and $SiO_2$ etched at much smaller rates of 0.03, 0.11 and 0.01 Å/min, respectively. Much higher Si etch rates were observed at higher HF pressures at 275 °C. The Si etch rate increased to 240 Å/min at an HF pressure of 9 Torr.

Si etch vs Si non-etch with co-adsorbed $H_2O$ illustrated the influence of polar co-adsorbed species on the etching. QMS experiments revealed that Si was etched by HF at a pressure of 1 Torr with a temperature threshold at ~150°C. In contrast, co-dosing $H_2O$ at a pressure of 1 Torr eliminated Si etching. These results suggest that $F^-$ is the active etch species for Si etching. QMS experiments also identified the volatile etch products as $H_2$ and $SiF_4$. $SiO_2$ non-etch vs $SiO_2$ etch with co-adsorbed $NH_3$ or $(CH_3)_2NH$ also supported the idea that polar co-adsorbates convert the HF active species to $HF_2^-$. Without polar co-adsorbates, $F^-$ species do not etch $SiO_2$. With polar co-adsorbates, $HF_2^-$ species can etch $SiO_2$.

2:30pm **AP+PS+TF-WeA-2 ZrO2 Thermal Atomic Layer Etching Using HF for Fluorination and TiCl4 for Ligand Exchange: Effect of Processing Parameters***, **Chen Li**, Troy Colleran,* University of Colorado Boulder*; Beomseok Kim, Hanjin Lim,* Samsung Electronics Co., Republic of Korea*; Steven George,* University of Colorado Boulder

$ZrO_2$ thermal atomic layer etching (ALE) can be performed using sequential surface modification and volatile release reactions. HF fluorinates the $ZrO_2$ surface to form a $ZrF_4$ layer. $TiCl_4$ then undergoes ligand-exchange and volatilizes the $ZrF_4$ layer. In this study, the etch rate of $ZrO_2$ ALE was evaluated as a function of various processing parameters such as pressure, temperature and exposure time. The initial $ZrO_2$ films were grown by atomic layer deposition (ALD) using tetrakis(diethylamino) zirconium and $H_2O$. The processing parameters during $ZrO_2$ thermal ALE were examined using various techniques including quartz crystal microbalance (QCM), x-ray reflectivity (XRR), atomic force microscopy (AFM) and quadrupole mass spectrometry (QMS).In situ QCM experiments examined $ZrO_2$ ALE at HF pressures from 0.1 to 0.9 Torr with fixed $TiCl_4$ pressure and at $TiCl_4$ pressures from 0.2 to 2 Torr with fixed HF pressure. The mass of the $ZrO_2$ film decreased linearly with number of ALE cycles. The higher HF and $TiCl_4$ pressures led to higher $ZrO_2$ etch rates. However, self-limiting behavior was observed at both low and high HF and $TiCl_4$ pressures. The $ZrO_2$ etching rates were also observed to increase at higher temperatures. These results illustrate that self-limiting reactions can occur over a range of reactant pressures and temperatures. At higher reactant pressures, the QCM analysis measured mass change per cycle (MCPC) values that varied from −49.4 to −118.6 ng/(cm$^2$ cycle) at 200 and 300 °C, respectively. These MCPCs correspond to $ZrO_2$ etch rates from 0.87 to 2.09 Å/cycle at 200 and 300 °C, respectively. XRR measurements also confirmed the linear removal of $ZrO_2$ versus number of ALE cycles and the etch rates. AFM measurements also studied the roughness of crystalline $ZrO_2$ films after ALE. These crystalline films contained a mixture of monoclinic and tetragonal phases. The surface roughness increased with number of ALE cycles. However, higher precursor pressures at high temperatures produced a lower roughness increase. In addition, QMS analysis revealed the volatile etch products during the sequential HF and $TiCl_4$ exposures on $ZrO_2$ at 200, 250 and 300 °C. The signal intensity of the etch products increased at higher temperatures. $H_2O$ was monitored during the HF exposure when HF fluorinates $ZrO_2$ to produce $ZrF_4$. $ZrCl_4$ was observed as the etch product and $TiFCl_3$ was detected as the ligand-exchange product during the $TiCl_4$ exposure. These products confirm the ligand-exchange reaction between $TiCl_4$ and $ZrF_4$.This project was supported by Samsung Electronics Co., Ltd (IO230707-06660-01).

2:45pm **AP+PS+TF-WeA-3 $SiO_2$ Etching by HF in a Liquid-Like $H_2O$ Layer in a Vacuum Environment***, **Samantha Rau**[1], Micah Duffield,* University of Colorado at Boulder*; Antonio Rotondaro, Hanna Paddubrouskaya, Kate Abel,* Tokyo Electron America, Inc.*; Steven George,* University of Colorado at Boulder

Adsorbed $H_2O$ layers may be employed for etching by a liquid layer in a vacuum environment. Liquid-like $H_2O$ layers can form at $H_2O$ pressures around 10 Torr and temperatures around room temperature. Etchants may then be dissolved in the liquid-like $H_2O$ layers. These conditions allow many etching processes that are conducted in wet aqueous solutions to be extended to liquid-like $H_2O$ layers in vacuum.

This study focused on $SiO_2$ etching by HF in a liquid-like $H_2O$ layer in vacuum. The experiments were conducted in a warm-wall vacuum chamber designed with a sample stage that allowed for $H_2O$ liquid layer formation only on the cooled stage. The thickness of $SiO_2$ films was measured using *in situ* spectroscopic ellipsometry as the $SiO_2$ films were exposed to various $H_2O$ and HF pressures at different substrate temperatures. Studies were conducted at $H_2O$ pressures from 5 to 30 Torr, HF pressures from 2 to 6 Torr, exposures time from 2 to 20 s, and temperatures from 18.1 to 30.4 °C. The $SiO_2$ films etched readily under these conditions.

The $SiO_2$ etch rate increased versus HF pressure. Figure 1 shows that as the HF pressure was increased from 2 to 6 Torr, at 30.4 °C with a $H_2O$ pressure of 15 Torr and exposure time of 5 s, the $SiO_2$ etch rate increased from ~14 Å/exposure to ~3315 Å/exposure, respectively. The $SiO_2$ etching also increased versus $H_2O$ pressure. Figure 2 shows that as the $H_2O$ pressure was increased from 10 to 30 Torr, at 30.4 °C with a HF pressure of 3.5 Torr and exposure time of 5 s, the $SiO_2$ etch rate increased from ~10 Å/exposure to ~105 Å/exposure, respectively. The dramatic variation in $SiO_2$ etch rates suggests that the thickness and composition of the liquid-like layer may be changing rapidly with HF and $H_2O$ pressure.

The $SiO_2$ etch rate also increased versus exposure time. As the exposure time increased from 2 to 20 s, at 30.4 °C with a $H_2O$ pressure of 10 Torr and HF pressure of 3.5 Torr, the $SiO_2$ etch rate increased from ~6 Å/exposure to ~150 Å/exposure, respectively. The $SiO_2$ etch rate was also inversely dependent on sample temperature. Experiments were conducted at temperatures of 30.4°C, 27.2°C, and 18.1°C with a $H_2O$ pressure of 15 Torr, HF pressure of 3.5 Torr, and exposure time of 5 s. These studies yielded $SiO_2$ etch rates of ~33 Å/exposure, ~1564 Å/exposure, and ~3456 Å/exposure, respectively. The large increase of the $SiO_2$ etch rate is attributed to the thicker liquid-like layer at lower temperatures. The thicker liquid-like layer may be able to more easily solvate the HF reactants and $SiO_2$ etch products.

3:00pm **AP+PS+TF-WeA-4 Wet-Like Atomic Layer Etching of WCN by Applying the Leidenfrost Effect to Obtain Floating Nanomist-Assisted Vapor Etching***, **Thi-Thuy-Nga Nguyen**,* Nagoya University, Japan*; Kazunori Shinoda, Kenji Maeda, Kenetsu Yokogawa, Masaru Izawa,* Hitachi High-Tech Corp., Japan*; Kenji Ishikawa, Masaru Hori,* Nagoya University, Japan

Semiconductor devices have been miniaturized to the nanometer scale. Work function metals, made from various metals like TiAlC, TiC, TiN, and WCN, are used in field effect transistor gate stacks. Precise control of isotropic and selective atomic layer etching (ALE) of thin metal gate materials in 3D nanostructures is crucial for the next-generation logic semiconductor devices. This requires minimizing damage from sputter effects in plasma ALE, high temperatures in thermal ALE, and pattern collapse in wet ALE. In our previous study, we developed a wet-like plasma etching method for a ternary metal carbide TiAlC [1]. This technique combines the advantages of wet etching (high isotropy and selectivity) and dry etching (high controllability). By using high-density vapor plasma at medium pressures, we generated a rich radical source of reactive species to significantly increase the reaction rate with the sample surface. This opens an avenue for developing our new dry ALE method, named wet-like ALE.

Here we have demonstrated the wet-like ALE for WCN material by sequentially exposing it to a rich radical source of $O_2$ plasma for surface oxidation at a relatively low temperature of less than 40 $^o$C and removal of the modified layer ($WO_3$) by dissolving it in a highly volatile nanomist flow. The proposed nanomist phase is a mist-vapor phase with properties between the mist liquid and vapor phases, maintaining the wet properties of the liquid phase at a minimal mist size for nanodevice applications. At the Leidenfrost point, the nanomist floats on its own stable vapor cushion film over the whole sample surface [2]. By using the Leidenfrost effect, the modified layer can be dissolved in a stable vapor film existing under the floating nanomist or in a floating nanomist-assisted vapor. The nanomists were generated from liquids by our originally developed non-contact atomizer at room temperature. The high removal rate of the modified layer ($WO_3$) was obtained at a temperature higher than 130 $^o$C that is considered as the Leidenfrost point of the nanomist produced from the aqueous liquid mixture, in which the WCN surface is supposed to be etched by the floating nanomist-assisted vapor at medium pressures. Self-limiting oxidation and removal of WCN by nanomist were achieved in both steps of the wet-like ALE cycle.

**Acknowledgement**

We would like to thank Dr. Yoshihide Yamaguchi (Hitachi, Ltd., Japan) and Mr. KuangDa Sun (Nagoya University) for the previous discussions about Leidenfrost effect and mist generation, respectively.

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3:15pm **AP+PS+TF-WeA-5 Thermal Atomic Layer Etching of Hafnium–Zirconium Oxide (HZO) Using Organofluorides for Fluorination***, **Aziz Abdulagatov**, Jonathan Partridge,* University of Colorado at Boulder*; Matthew Surman,* ASM Microchemistry Ltd., Finland*; Steven George,* University of Colorado at Boulder

Thermal atomic layer etching (ALE) of various materials has previously been achieved using sequential fluorination and ligand exchange reactions where HF has been used as the fluorination source.In this work, organofluorides were employed as an alternative to HF.The thermal ALE of $Hf_{0.5}Zr_{0.5}O_2$ (HZO) was demonstrated using various organofluorides.The organofluorides were N,N-Diethyl-1,1,2,3,3,3-hexafluoropropylamine (Ishikawa's reagent (IR)), 1,1,2,2-tetrafluoroethyldimethylamine (TFEDMA) and diethylaminosulfur

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[1] **JVST Highlighted Talk**

trifluoride (DAST). IR, TFEDMA and DAST are common deoxyfluorination reagents.

HZO ALE was demonstrated using organofluoride exposure in combination with ozone ($O_3$) and boron trichloride ($BCl_3$) exposures. Ozone was used to remove carbon residue resulting from organofluoride adsorption. $BCl_3$ was employed for ligand exchange with the fluorinated surface to form volatile Hf and Zr chlorides and $BCl_xF_y$ products. $BCl_3$ can also undergo conversion with HZO.

*In situ* spectroscopic ellipsometry (SE) observed the linear decrease of HZO film thickness. Under similar reaction conditions at 270 °C, crystalline HZO films with a thickness of 10 nm displayed etch rates of 0.1, 0.2, and 0.5 Å/cycle, using IR, TFEDMA, and DAST, respectively. Etching amorphous HZO using IR yielded higher etch rates of 0.6 Å/cycle at 270 °C. The IR, $O_3$ and $BCl_3$ surface reactions were also determined to be self-limiting.

Quadrupole mass spectrometry (QMS) was also utilized to study the IR-$O_3$-$BCl_3$ etch process on crystalline $ZrO_2$ powder at 270°C. During IR exposure, organic fragments and HF were detected indicating that HF is produced in situ by IR at 270 °C.During $O_3$ exposure, combustion products were observed from the oxidation of organic residuals left from IR exposures. During $BCl_3$ exposure, Hf and Zr chloride products, as well as $BCl_xF_y$ products, were produced by the ligand-exchange reactions. Concurrently, boroxine ring ($B_3O_3Cl_3$) fragments were monitored and indicated the conversion of HZO to $B_2O_3$.

3:30pm **AP+PS+TF-WeA-6 Selective Atomic Layer Etching of $SiO_2$ over $Si_3N_4$ via TMA Surface modification and SF6 Remote Plasma**, ***Jieun Kim****, Min Kyun Sohn, Sun Kyu Jung, Min-A Park, Jin Ha Kim, Jaeseoung Park, Subin Heo, Sang-Hoon Kim, Jeong Woo Park, Seong Hyun Lee, Dongwoo Suh,* Electronics and Telecommunications Research Institute, Republic of Korea

Precise etch selectivity between $SiO_2$ and $Si_3N_4$ is critical in advanced semiconductor fabrication processes, especially for applications such as spacer patterning in Gate-All-Around Field-Effect Transistors (GAAFETs) and multilayer structuring in 3D NAND devices. While selective etching of $Si_3N_4$ over $SiO_2$ has been widely studied using plasma chemistries such as $SF_6/H_2/Ar/He$, $NF_3/O_2$, and $CF_4/O_2/N_2$ gas mixtures,[1-3] achieving atomic-scale precision in the reverse case —preferentially etching $SiO_2$ over $Si_3N_4$— remains challenging.

In this work, we present an atomic layer etching (ALE) approach that enables highly selective etching of $SiO_2$ over $Si_3N_4$ through surface chemical engineering. The process sequence comprises four steps — trimethylaluminum (TMA) surface modification, Ar purge, $SF_6$ remote plasma exposure, and Ar purge— perfomed at 300 °C, 5 Torr, with an $SF_6$ flow rate of 50 sccm.

Under standard $SF_6$ plasma conditions, $Si_3N_4$ is typically etched more rapidly than $SiO_2$ due to the greater susceptibility of Si–N bonds to fluorine radicals. However, we found that incorporating a TMA surface modification step effectively inverts this trend. Chemical interactions at the surface are believed to yield Al–O–Si linkages on $SiO_2$ and Al–N–Si on $Si_3N_4$, leading to distinct reactivities during subsequent F-radical exposure. The Al–O–Si sites promote the formation of volatile $AlF_3$ and $SiF_4$, whereas Al–N–Si structures exhibit much lower fluorine reactivity.

This chemistry-driven mechanism enabled a marked difference in etch per cycle EPC, with $SiO_2$ reaching 0.49 Å/cycle and $Si_3N_4$ reaching 0.05 Å/cycle, resulting in a selectivity close to 10:1. Whereas conventional atomic layer plasma etching using $CH_2F_2/O_2/N_2$ gas mixtures achieves selectivity through physical passivation or polymer deposition—often leading to surface damage or limited thickness control—our method, based on surface chemical modification and remote plasma exposure, enables damage-free etching and precise, layer-by-layer thickness control by decoupling chemical reactivity from ion bombardment. These findings suggest that surface modification-based selectivity tuning can serve as a viable strategy for precision etching in next-generation logic and memory device integration.

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4:15pm **AP+PS+TF-WeA-9 Mitigating Redeposition in Directional Atomic Layer Etching of Lithium Niobate Using HBr Plasma***, Ivy Chen,* Caltech*; Frank Greer,* Jet Propulsion Laboratory (NASA/JPL)*; **Austin Minnich**,* Caltech

Lithium niobate (LiNbO3, LN) is a ferroelectric crystal of interest for integrated photonics owing to its large second-order optical nonlinearity and the ability to impart periodic poling via an external electric field. However, on-chip device performance based on thin-film lithium niobate (TFLN) is presently limited by propagation losses arising from surface roughness and corrugations. Atomic layer etching (ALE) could potentially smooth these features and thereby increase photonic performance. Previously, our group has reported the first isotropic ALE processes for lithium niobate. Here, we report a directional ALE process for x-cut MgO-doped LN using an HBr-containing plasma. At 0 degrees Celsius we report an 85% synergy ALE recipe with etch rate of 1.1 nm/cycle and surface roughening. At 200 degrees Celsius we report a reduced synergy at 30%, with an etch rate of 1.24 nm/cycle and no evidence of surface roughening. We also compare the surface roughness result of the HBr containing process with a chlorine-only process. Our ALE process could be to fabricate waveguide structures with nanometer precision without surface roughening or redeposition, thereby increasing the performance of TFLN nanophotonic devices and enabling new integrated photonic device capabilities.

4:30pm **AP+PS+TF-WeA-10 Atomic Layer Etching of Sputter-Deposited AlN Thin Films in Cl2-Ar Plasmas***, Iurii Nesterenko*[1]*,* Silicon Austria Labs GmbH, Austria*; Jon Farr,* Applied Materials, Inc.*; Steffen Harzenetter,* Applied Materials, Inc., Germany*; Dmytro Solonenko, Benjamin Kalas, Thang Dao,* Silicon Austria Labs GmbH, Austria*; Julian Schulze,* Ruhr University Bochum, Germany*; **Nikolai Andrianov**,* Silicon Austria Labs GmbH, Austria

Aluminum nitride (AlN) is a widely used material in micro- and nanoelectronics, particularly in photonics and MEMS devices. However, one of the critical challenges in the fabrication of AlN-based devices is achieving precise nanoscale etching while maintaining smooth surfaces and well-defined etch profiles. Atomic Layer Etching (ALE) is a promising approach the above-mentioned problems, which are particularly crucial in photonic applications, where surface roughness and deviations in profile angles can result in optical losses and inefficient mode confinement.

This study investigates the ALE of AlN thin films deposited via sputter deposition on an 8-inch wafer. The wafer was diced into 2 × 2 cm coupons, which were then attached to a $SiO_2$ thermal oxide carrier wafer. The experiments were performed in an Applied Materials™ Centura™ DTM Chamber using $Cl_2$ and Ar gases for the modification (Cl step) and ion bombardment (Ar step) steps, respectively. The thickness of the AlN thin films was measured via spectroscopic ellipsometry (Semilab SE-2000). Also, the ion energy distribution function (IEDF) was analyzed using an ion energy analyzer (Impedance Quantum).

The feasibility of ALE for sputter-deposited AlN thin films was successfully demonstrated. The etch per cycle (EPC) was found to be approximately a single monolayer of the wurtzite AlN crystal structure (Fig.1). The ALE energy window was determined by analyzing the IEDFs in the Ar step, revealing the energy range of around 75 eV, which is consistent with the previously reported data in the literature [1]. Furthermore, measurements of the AlN sputtering threshold under Ar bombardment (Fig. 1) indicated minimal sputtering contributions, suggesting that the synergy of the process could approach 100%. Further investigations will be conducted to quantify this synergy more accurately. Moreover, it was determined that the process is linear, e.g. the EPC is constant against the number of cycles (Fig.2). The AlN RMS roughness after processing within the ALE energy window is around 570pm (Fig.3), which is lower than the original material roughness of 3nm.

Future work will also focus on optimizing the process by minimizing the duration of the Ar, Cl, and purge steps. The optimization of the Cl step will be complemented by X-ray Photoelectron Spectroscopy (XPS) to gain deeper insights into the surface chlorination mechanism.

[1] T. Faraz, Y. G. P. Verstappen, M. A. Verheijen, N. J. Chittock, J. E. Lopez, E. Heijdra, W. J. H. Van Gennip, W. M. M. Kessels, and A. J. M. Mackus, Precise ion energy control with tailored waveform biasing for atomic scale processing, Journal of Applied Physics **128**, 213301 (2020).

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[1] **JVST Highlighted Talk**

4:45pm **AP+PS+TF-WeA-11 Sub-Surface TiO2 Atomic Layer Etching (ALE) Through W Films***, **Hannah Margavio**, Gregory Parsons,* North Carolina State University

The growing complexity of microelectronic architectures requires the development of novel atomic-scale fabrication techniques. Traditional semiconductor processing relies on separate deposition and etching steps. For example, a common fabrication technique known as etch-replacement deposition proceeds with W atomic layer deposition (ALD) and $TiO_2$ chemical vapor etching (CVE) occurring locally via $SiH_4$ and $WF_6$ exposure, yielding a W film thickness roughly equal to the removed $TiO_2$ film. In the etch replacement process, $WF_6$ converts $TiO_2$ into an intermediate solid phase, $TiWO_xF_y$, which becomes volatile upon further $WF_6$ exposure. Alternatively, $TiWO_xF_y$ can be reduced by $SiH_4$, resulting in a W-rich film.

In this work, we address the need for advanced and unique processing for more complex metal nanostructures using atomic layer etching (ALE). We demonstrate the fabrication of intricate metal architectures via sub-surface etching of $TiO_2$ by controlling $WF_6$, $MoF_6$, and $BCl_3$ etching conditions after W ALD. First, 30 W ALD cycles were deposited on $TiO_2$/Si line patterns resulting in ~20 nm of W deposition on $TiO_2$. Following deposition, the film stack was exposed to 10, 80, and 150 $WF_6$ individual doses. After $WF_6$ exposure, it was found the W layer remained and the underlying $TiO_2$ layer was etched away as a function of CVE cycles, creating an air gap between the patterned $TiO_2$ lines and the W layer. We will show when additional $WF_6$ doses were exposed to the film stack, the air gap spacing increased. Similarly, $MoF_6$ doses after W ALD initiated sub-surface $TiO_2$ CVE. With $MoF_6$, we were able to elucidate the sub-surface etching mechanism via STEM EDS mapping; we observed metal fluoride diffused through the W film to react with the underlying $TiO_2$, while etch products diffused out. Compared to $WF_6$ and $MoF_6$ driven CVE, ALE using sequential $WF_6$ and $BCl_3$ doses accelerated etching and allowed greater control of $TiO_2$ removal. By integrating W ALD and $TiO_2$ ALE with sequential $WF_6$ and $BCl_3$ cycles on patterned $TiO_2$ structures, unique film stacks with tunable, uniform air gaps were fabricated.

5:00pm **AP+PS+TF-WeA-12 Pulsed Plasma Strategies for High-Precision Pseudo-Atomic Layer Etching***, **Maryam Khaji**,* University of Michigan*; Qinzhen Hao, Mahmoud A. I. Elgarhy, Jeremy Mettler,* University of Houston*; Hyunjae Lee, Sang Ki Nam,* Mechatronics Research, Samsung Electronics Co, Republic of Korea*; Vincent Donnelly,* University of Houston*; Mark J. Kushner,* University of Michigan

Conventional plasma-based atomic layer etching (ALE) involves two self-limiting steps: passivation, where radicals (e.g., Cl) passivate the top layer of the substrate (e.g., silicon) to form $SiCl_x$; and etching, where the passivated layer is selectively removed by an ion-rich flux with its energy tuned to etch only the passivated material [1]. In spite its high precision, ALE is time-consuming due to the need to evacuate the chamber between steps and so is challenged to incorporate into high volume manufacturing (HVM). Strategies are needed to maintain the precision of ALE while increasing its processing speed.

In this work, we report on a computational investigation of strategies to achieve rapid and precise Pseudo-Atomic Layer Etching (P-ALE) processes. This investigation is conducted for an inductively coupled plasma (ICP) reactor with RF or dc power applied to the substrate using Ar/$Cl_2$ mixtures for Si etching. Reactor scale plasma properties are addressed using the Hybrid Plasma Equipment Model (HPEM). Feature profile evolution is evaluated using the Monte Carlo Feature Profile Model (MCFPM) [2].

We will discuss strategies for P-ALE whose goal is to maintain the dual-process (passivation-etching) of conventional ALE while using a single gas mixture. These strategies use combinations of pulsed source (ICP) and bias powers, and electrode biasing, that produce a passivation phase where ion energies are low, and that appears to be ion starved; followed by rapid etch phase where additional passivation is low, and that appears to be neutral starved. To achieve these ends, plasma potential and dc bias must be carefully managed. Comparisons are made to experimental data.

This work was supported by Samsung Electronics and the Department of Energy Office of Fusion Energy Sciences.

[1] C. Huard et al., J. Phys. D: Appl. Phys. 51 155201 (2018)

[2] C. Huard et al., J. Vac. Sci. Tech. A 35, 05C301 (2017).

5:15pm **AP+PS+TF-WeA-13 Development of Atomic Layer Etching Process Dedicated to Diamond Electronic Devices***, **Marine Régnier**,* Univ. Grenoble Alpes, CNRS, Grenoble INP, Institut Néel; Institute of Applied Physics, University of Tsukuba; Japanese-French Laboratory for Semiconductor Physics and Technology J-FAST, CNRS, Univ. Grenoble Alpes, University of Tsukuba, France*; Aboulaye Traoré,* LSPM, CNRS, Université Sorbonne Paris Nord, France*; Marceline Bonvalot,* Univ. Grenoble Alpes, CNRS, Grenoble INP, LTM; Japanese-French Laboratory for Semiconductor Physics and Technology J-FAST, CNRS, Univ. Grenoble Alpes, University of Tsukuba, France*; Etienne Gheeraert,* Univ. Grenoble Alpes, CNRS, Grenoble INP, Institut Néel; Institute of Applied Physics, University of Tsukuba; Japanese-French Laboratory for Semiconductor Physics and Technology J-FAST, CNRS, Univ. Grenoble Alpes, University of Tsukuba, France

Diamond power devices, such as Schottky diodes and MOSFETs are currently being intensively investigated for possible application in power electronics and require dedicated fabrication processes to achieve adequate operating performances. Conventional etching techniques often lead to defects, surface roughness and sub-surface damages, which can significantly degrade carrier mobility and breakdown voltage of power devices. Thus, it becomes essential to develop diamond etching processes minimizing induced defects. Atomic layer etching (ALE) is a very soft etching technique involving two successive self-limiting and independent reactions. The first self-limiting reaction involves modifying the surface of a material by forming an ultra-thin reactive surface layer, while the second self-limiting reaction consists in the sputtering of the modified layer while keeping the underlayer intact. The repetition of these two reactions allows the removal of a layer of materials with a defect-free etched surfaces and sub-surfaces at atomic-scale precision. The first report of ALE of diamond dates back to 1988 [1], however, since then, no further studies have been reported.

In this work, the ALE process optimization of (100) diamond is presented. The ALE process is achieved by first modifying the surface and then using a soft plasma to induce the selective removal of this modified surface. Experiments have been performed in a standard inductively coupled plasma reactive ion etching equipment with in-situ plasma monitoring by optical emission spectroscopy. They have been characterized as a function of the etching rate per cycle (EPC) estimated from diamond etched depth after 100 ALE cycles. The impact of the incident ionic bombardment kinetic energy during the 2nd ALE reaction has been evaluated from the dc self-bias voltage ($V_{DC}$). Results show a clear plateau of approximatively 5 V (Fig. 1), called ALE window, demonstrating the self-limiting effect of the etching process within one ALE cycle. The etching rate is of 7.1 Å per cycle, corresponding to the removal of two (100) diamond monolayers per cycle. Finally, synergy factor has been calculated. Synergy measures the effect of combining the two ALE steps. Separately, 100 cycles of step 1 then 100 cycles of step 2 leads to an etching rate of 4.0 Å per cycle. But 100 cycles of (1+2) steps lead to 7.1 Å per cycle, *i.e.* a synergy of 43%. This again demonstrate the effectiveness of the ALE process.

All these results will be presented in detail and discussed in the light of literature data.

**References**

[1]M.N. Yoder, Atomic Layer Etching, US4756794A, 1988.

5:30pm **AP+PS+TF-WeA-14 Atomic Layer Etching for Vertical Trench Control and Electrical Optimization in HDLK Materials***, **Sanghyun Lee**, Keun Hee Bai,* Samsung Electronics, Republic of Korea

As device scaling continues, it becomes increasingly challenging to enhance device performance. In order to improve device performance, reducing resistance and capacitance in the BEOL (Back-End of Line) is especially important. Among various methods, minimizing damage to low-k dielectric materials during patterning processes has become a key challenge in BEOL integration. In this work, we suggest using Atomic Layer Etching (ALE) to overcome this problem, along with the selection of suitable low-k materials. ALE enhances controllability over surface reactions and profile formation by utilizing low ion energy, which enables the achievement of vertical profiles while simultaneously minimizing Plasma-Induced Damage (PID). The proposed ALE process utilizes a fluorocarbon-based surface modification step ($C_4F_8$), followed by a low-energy $O_2$ plasma step for selective carbon removal. This cyclic approach enables atomic-scale material removal with minimal physical damage, significantly reducing ion bombardment effects. To evaluate the effect of ALE on different low-k materials, we tested various High-Density Low-k (HDLK) samples with differences in k-value, modulus, and carbon composition. As a result, both low-k damage and vertical trench profile integrity were substantially improved, with smoother sidewalls and better verticality observed. The process performance was evaluated through detailed compositional analysis (XPS, EDX), PID characterization, and electrical measurements. The results confirmed that the proposed ALE method effectively reduced damage to low-k materials while enhancing profile control. Consequently, it demonstrates strong potential as a next-generation patterning solution for advanced BEOL integration.

5:45pm **AP+PS+TF-WeA-15 Mechanisms of Atomic Layer Etching of Ni3Al**, ***Owen Watkins**, Taylor G. Smith,* University of California, Los Angeles*; Jean-François de Marneffe,* IMEC, Belgium*; Jane P. Chang,* University of California, Los Angeles

New metals and alloys are being investigated as potential replacements to TaBN in the absorber layer of extreme ultraviolet (EUV) lithography masks. Among potential candidates, $Ni_3Al$ is particularly promising because it has both a high extinction coefficient and an index of refraction close to 1. A major hurdle in integration is anisotropically etching $Ni_3Al$ selective to Ru, the 2-3 nm capping layer underneath the $Ni_3Al$ absorber, with previously developed reactive ion etch and oxygen plasma-based atomic layer etch (ALE) having selectivities of 0.4 and 0.6, respectively. Better selectivity could be obtained through an ALE process based on cycles of nitrogen plasma, which does not spontaneously form volatile Ru compounds.

In this work, a $Ni_3Al$ ALE process using nitrogen plasma, formic acid vapor, and $Ar^+$ ion beam sputtering is investigated. The three step ALE process was shown to etch blanket $Ni_3Al$ films at a rate of 1.0 nm/cycle. The self-limiting nature of the ALE process was examined by varying the duration of the nitridation, FA vapor, and $Ar^+$ ion beam steps one at a time and measuring the resulting etch rate per cycle after 10 ALE cycles. These experiments showed that increasing the low energy $Ar^+$ ion beam served only to remove residual formate from the surface prior to starting the subsequent ALE cycle and was not responsible for etching the $Ni_3Al$. The anisotropy of the $Ni_3Al$ ALE process was examined using specially prepared samples of $Ni_3Al$ deposited over patterned Si which had an initial sidewall $Ni_3Al$ thickness of 17 nm. Scanning electron microscopy (SEM) showed that 30 ALE cycles redeposited material on the feature sidewalls, increasing the sidewall thickness to 34 nm at the bottom of the patterned feature and 21 nm near the top. The etch mechanism, particularly the volatile Al product, was investigated by comparing the etch rates of Ni, $Ni_3Al$, NiAl, and Al films. Ni etched at a rate of 1.3 nm/cycle[1] and $Ni_3Al$ at a rate of 1.0 nm/cycle, while NiAl and Al were not etched by this ALE process. Because films with high Al content did not etch, Ni clearly plays a role in the removal of Al. Possible volatile etch products of Al therefore include a dimeric complex containing both a Ni and Al atom, or trimethylaluminum from Al reacting with $CH_3$ formed by Ni-catalyzed hydrogenation of formic acid. Finally, the etch rate of blanket Ru films was determined to be 0.5 nm/cycle, demonstrating a 2:1 selectivity between $Ni_3Al$ and Ru—a major advance toward integration of $Ni_3Al$ in EUV masks.

[1] T.G. Smith, A.M. Ali, J.F. de Marneffe, J.P. Chang, *JVST A* **42**, 022602 (2024).

6:00pm **AP+PS+TF-WeA-16 In-situ Comparative Analysis of Surface Reactions During Isotropic Atomic Layer Etching of TiC under Various Plasma Chemistries and Infrared Heating**, ***Kazunori Shinoda**,* Hitachi High-Tech Corporation, Japan*; Thi-Thuy-Nga Nguyen,* Nagoya University, Japan*; Dai Ishikawa, Kenetsu Yokogawa, Masaru Izawa,* Hitachi High-Tech Corporation, Japan*; Kenji Ishikawa, Masaru Hori,* Nagoya University, Japan

As integration density increases, field-effect transistors (FETs) have evolved from two-dimensional planar structures to three-dimensional FinFETs, with gate-all-around (GAA) structures now emerging at advanced technology nodes. To enable continued scaling, complementary FETs (CFETs) are being investigated as the next step beyond GAA. This structural progression has intensified interest in isotropic atomic layer etching (ALE), which offers atomic-level dimensional control critical for fabricating advanced three-dimensional semiconductor structures. In response to this demand, a thermal-cyclic ALE process has been developed, incorporating cyclic plasma exposure and infrared (IR) heating for surface modification and layer removal. A 300-mm dry chemical removal (DCR) tool was engineered to implement this process. Using this system, selective isotropic ALE has been demonstrated for materials including $Si_3N_4$, $SiO_2$, TiN, W, and Co. This study presents a comparative analysis of surface atomic-layer reactions during TiC ALE using various fluorocarbon-based plasma chemistries. In-situ X-ray photoelectron spectroscopy (XPS) was employed to characterize surface chemical bonding states, while in-situ spectroscopic ellipsometry was used to monitor etching performance during cyclic processing. The experimental setup comprised a radical irradiation chamber and an XPS analysis chamber, connected via a high-vacuum transfer system to preserve surface integrity. Exposure to radicals generated from fluorocarbon-based gas mixtures resulted in the formation of surface-modified layers containing Ti–F bonds. Exposure to radicals generated from nitrogen-containing fluorocarbon-based gases led to the appearance of N–H bonds, with a binding energy centered at 402 eV. This reaction pathway is analogous to that observed in TiN ALE, where the surface-modified layer was tentatively identified as containing ammonium salt-based species. These layers were effectively removed by IR heating. Repetitive cycles of plasma exposure and IR heating produced a linear increase in TiC etching depth with cycle count. The etch per cycle (EPC) varied with plasma chemistry, typically ranging from 0.9 to 1.4 nm/cycle under optimized conditions. Saturation behavior with respect to radical exposure time confirmed the self-limiting nature of the process. Throughout the ALE cycles, the etched TiC surfaces remained smooth.

## Electronic Materials and Photonics

## Room 207 A W - Session EM1+AP+CPS+MS+PS+SM+TF-WeA

### Materials and Devices in Emerging Memories

**Moderators: M. David Henry**, Sandia National Labs, **Philip Lee**, University of Kentucky

2:15pm **EM1+AP+CPS+MS+PS+SM+TF-WeA-1 Impact of Precursor Purge Time on the Performance of Ferroelectric Hf0.5Zr0.5O2 Prepared by Plasma-Enhanced Atomic Layer Deposition**, ***Yong Kyu Choi**, Benjamin Aronson, Megan Lenox, Liron Shvilberg,* University of Virginia, USA*; Chuanzhen Zhou,* North Carolina State University*; Kristina Holsgrove,* Queen's University Belfast, UK*; Amit Kumar,* Queen's University Belfast, UK*; Andrea Watson, Stephen J. McDonnell, Jon F. Ihlefeld,* University of Virginia, USA

Hafnium oxide ($HfO_2$) shows significant potential for non-volatile memory and energy harvesting applications. However, its monoclinic phase lacks polarization, making it unsuitable for ferroelectric applications. Introducing $ZrO_2$ into $HfO_2$ (HZO) helps stabilize a ferroelectric phase. Atomic layer deposition (ALD) is the most widely used film processing technique, offering excellent thickness control, conformability, and relatively low processing temperature. Previous research has explored the impact of various metal precursors, oxidizer precursors, and process temperatures on the ferroelectric properties of HZO. One common observation is that the metal precursor purge time has a large effect on the resulting film phase and performance. However, no clear mechanism has been identified to explain this effect. In this presentation, we will discuss how HZO thin film properties change when the metal precursor purge time varies during plasma-enhanced ALD. Reducing the metal precursor purge time from 90 s to 3 s induced a transition from ferroelectric to antiferroelectric properties with double polarization hysteresis loops, higher endurance and polarization stability, and slightly increased in relatively permittivity. Infrared spectroscopy measurements (FTIR-ATR) confirmed that the antiferroelectric properties are due to the antipolar orthorhombic o-I phase, which is consistent with observations from HRTEM and DPC-STEM. The films deposited with shorter purge times showed carbon impurities as identified by ToF-SIMS analysis. This suggests that residual chemical ligands from incomplete precursor removal during the ALD process, in part, stabilizes the antipolar o-I phase. These results show that phase stability in fluorite oxides is influenced by impurities beyond intentional substituents and that stable antiferroelectric responses can be achieved without deliberately altering the material composition, such as adjusting the Hf:Zr ratio to control phase formation.

2:30pm **EM1+AP+CPS+MS+PS+SM+TF-WeA-2 Effect of Atomic Layer Annealing Duration on Phase Stabilization of Hafnium Zirconium Oxide Thin Films**, ***Nicolas Lam**,* University of Virginia*; Gerald Bejger, John Barber,* Virginia Tech*; Megan Lenox, Liron Shvilberg,* University of Virginia*; Christina Rost,* Virginia Tech*; Jon Ihlefeld,* University of Virginia

Significant research has gone into understanding the stabilizing mechanisms and properties of ferroelectric hafnia. This is largely due to its ability to display ferroelectricity in size scales below 10 nm, incorporation in already existing mass production infrastructure, and complementary metal oxide semiconductor compatibility. Today, hafnium zirconium oxide (HZO) is the most studied hafnia alloy due to its low processing temperature. However, the widespread implementation of HZO as a memory material is hindered by a variety of challenges, such as wake–up, imprint, and retention. A major issue is the inability to make phase pure ferroelectric HZO, a metastable non–centrosymmetric polar orthorhombic structure.

Commonly cited impurity phases include the metastable tetragonal, antipolar orthorhombic, and equilibrium monoclinic phases. Previous work using the atomic layer annealing (ALA) technique has shown enhanced crystallinity and remanent polarization in pristine HZO films, circumventing significant formation of the antiferroelectric and tetragonal phases. In this work, thin films of HZO were grown using the ALA technique with various ALA treatment durations, ranging from 0 s up to 59 s. Following a deposition of a metal oxide layer using plasma–enhanced atomic layer deposition, the surface of the film was subjected to additional argon plasma. After synthesis and a post–metallization anneal to form the metastable phase, various structural and electrical measurement techniques were used to characterize the films. Grazing-incidence X-ray diffraction shows no formation of the equilibrium monoclinic phase; Fourier transform infrared spectroscopy shows increasing ferroelectric phase concentration with ALA time. Polarization hysteresis measurements show an increasing hysteretic response with ALA time as compared to an antiferroelectric reference sample. Positive up negative down measurements quantified the relative amount of wake–up. The reference devices displayed a 200% increase in remanent polarization while the ALA samples displayed an 8% relative increase with the longest treatment time. The results suggest that ALA can modify the local environment of the deposited films, such that the phase fraction of the ferroelectric phase and the amount of wake–up can be tuned. This results in devices that exhibit minimal to no wake–up. This work furthers the understanding of the effect that ALA has on the resultant film's properties.

2:45pm **EM1+AP+CPS+MS+PS+SM+TF-WeA-3 Understanding Time-Dependent Imprint in Hafnium Zirconium Oxide Based Ferroelectric Tunnel Junctions*, Megan Lenox,*** University of Virginia, USA*; Samantha Jaszewski,* Sandia National Laboratories*; Jon Ihlefeld,* University of Virginia, USA*; M. David Henry,* Sandia National Laboratories, USA

While research into understanding the performance-materials property relationship of hafnium zirconium oxide (HZO) based devices has been accelerated in the past decade, their integration into microelectronic products is challenged by their endurance and imprint behavior. Imprint, or a shift in the coercive field following polarization with an initial applied field, lowers HZO remanent polarization ($P_r$) along the imprint direction, impacting the current transport mechanisms and reducing the overall performance stability when studied in ferroelectric non-volatile memory applications. In these devices, imprint has been hypothesized to result from charge carrier migration at the electrode interface, increasing the charge needed for polarization switching. However, the mechanisms responsible for imprint in ferroelectric tunnel junctions (FTJ) is not understood. To study FTJ imprint phenomena, 7 nm $Hf_{0.7}Zr_{0.3}O_2$ devices with NbN and Nb as the top and bottom electrode, respectively, were fabricated. Polarization-electric field measurements were performed every $2^n$ seconds, showing a $+V_c$ shift with time.

Resistance measurements, using a pulsing scheme composed of a $\pm V_{-max}$ write pulse followed by fifty 0.4 V read pulses at various pulse widths taken every $2^n$ seconds, showed a drift in the ratio of high and low resistance states, and an overall reduction in the binary state memory window with increasing time, characteristic of imprint. Further, these results highlight imprint impacts on multi-state polarization switching used in neuromorphic memory applications. To investigate imprint mechanisms, pulsed hysteresis measurements taken in 0.1 V intervals followed by a reset pulse at $\pm V_{-max}$ showed an 18.1x change in the resistance ratio between the high and low resistance states. However, a similar pulsed hysteresis measurement without the reset pulse had a 11.4x resistance ratio. These results support the generation of time-dependent imprint-free HZO-based FTJs by utilizing selective pulsing schemes, promoting their use in next-generation microelectronics.

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia LLC, a wholly owned subsidiary of Honeywell International Inc. for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525. This work is supported by the Center for 3D Ferroelectric Microelectronic Manufacturing (3DFeM2), an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences Energy Frontier Research Centers program under Award Number DE–SC0021118.

3:00pm **EM1+AP+CPS+MS+PS+SM+TF-WeA-4 Disentangling Gamma-Ray Radiation Effects and Time-Dependent Imprint on Ferroelectric Hafnium Zirconium Oxide-Based Devices*, Samantha Jaszewski,*** Sandia National Laboratories*; Megan Lenox, Jon Ihlefeld,* University of Virginia*; M. David Henry,* Sandia National Laboratories

Ferroelectric hafnium oxide ($HfO_2$) enables technological developments in microelectronics, such as the scaling of ferroelectric random-access memory (FeRAM) and new devices like ferroelectric field-effect transistors (FeFETs) and ferroelectric tunnel junctions (FTJs) that were not previously possible with conventional ferroelectrics. This is due to the material's compatibility with silicon and its ability to exhibit a ferroelectric response in films as thin as 1 nm. Understanding the interaction between radiation and ferroelectric $HfO_2$-based devices is necessary before these devices can be utilized in radiation-hostile environments. In the literature, it has been reported that gamma-ray radiation can result in a shift of the coercive voltage of ferroelectric $HfO_2$-based devices, impacting the memory window and, thus, the reliability of these devices. However, ferroelectric $HfO_2$-based capacitors have also been shown to exhibit a time-dependent imprint effect in which the coercive voltage shifts over time as a result of the depolarization field in the film, which drives charge redistribution in the ferroelectric layer. As such, it can be challenging to disentangle the effects of gamma-ray radiation and the time-dependent imprint shift when evaluating the performance of these devices.

In this work, ferroelectric hafnium zirconium oxide (HZO) capacitors and ferroelectric tunnel junctions (FTJs) are subjected to 1 and 5 Mrad doses of gamma-ray radiation under grounded and biased conditions. X-ray diffraction and Fourier-transform infrared spectroscopy measurements demonstrate that gamma-ray radiation does not result in phase transformations, further confirmed by capacitance-voltage measurements, which show that the relative permittivity of the HZO capacitors does not change after radiation. Polarization-electric field measurements show shifts in the coercive field after radiation. However, it will be shown that these coercive voltage shifts are due to time-dependent imprint in the material rather than the effects of gamma-ray radiation. This work demonstrates that the structural and electrical properties of ferroelectric HZO-based capacitors and FTJs are not affected by gamma-ray radiation up to doses of 5 Mrad. It also underscores the importance of careful measurement procedures and analysis when evaluating radiation effects in this material.

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## Electronic Materials and Photonics
## Room 207 A W - Session EM2+AP+NS+TF-WeA

### Advances in Materials and Devices for Energy Storage

**Moderators: Claire Davis-Wheeler Chin**, Sandia National Lab, **Alexander Kozen**, University of Vermont

3:15pm **EM2+AP+NS+TF-WeA-5 In-Situ Characterisation of Solid Electrolyte Interphase Formation on Lithium Metal for Energy Storage*, Anthony Somers,*** Deakin University, Australia

The Solid Electrolyte Interphase (SEI) is a complex passivating layer that forms on the anode in the early stages of battery cycling. Ideally this layer should protect the anode from degradation while allowing the ions of interest to freely move through with high efficiency. To ensure long cycle life this layer also needs to be stable over hundreds of charge/discharge cycles. For the safe and successful operation of promising new battery technologies, such as lithium metal, information on how electrolyte composition effects the SEI is needed.

Most analysis of the SEI is ex-situ, making it difficult to identify the processes occurring during the initial formation phase. While there are a range of in-situ and operando techniques that have been used to investigate SEI formation, there is often a lack of cross-checking between techniques to confirm findings or determine all processes involved.

In this work a range of in-situ, operando and ex-situ techniques have been used to identify the mechanisms of SEI formation in relation to cycling performance for lithium metal batteries with ionic liquid containing electrolytes. To achieve this, techniques able to detect early subtle changes at the electrode, such as electrolyte rearrangement and organic adsorption, as well as the final reactions that lead to the formation of inorganic, passive layers have been used. Measurements such as operando FTIR spectra, in-situ differential capacitance and electrochemical quartz crystal microbalance and ex-situ XPS are used to form this more complete picture of the processes involved in SEI formation.

3:30pm **EM2+AP+NS+TF-WeA-6 Intercalation of Polyacrylonitrile Nanoparticles in Ti3C2 MXene Layersfor Improved Supercapacitance**, ***Shanna Marie Alonzo***, *Bishnu Bastakoti,* North Carolina A&T State University

We report the intercalation of polyacrylonitrile nanoparticles in $Ti_3C_2T_x$ MXene layers through simple sonication. The use of polyacrylonitrile, which was synthesized via radical polymerization, offered dual benefits: (1) It increased the interlayer spacing ofMXene, thereby exposing more surface area and enhancing ion transport channels during charge and discharge cycles, and (2) Integrating MXene with polyacrylonitrile enables the creation of a composite with conductive properties, following percolation principle. X-ray diffraction analysis showed an increase in the c-lattice parameter, indicative of the interlayer spacing, from 22.31 Å for the pristine MXene to 37.73 Å for the MXene–polyacrylonitrile composite. The intercalated polyacrylonitrile nanoparticles facilitated the delamination by weakening the interlayer interactions, especially during sonication. Electrochemical assessments revealed significant improvement in the properties of the MXene–polyacrylonitrile composite compared to the pristine MXene. The assembled asymmetric device achieved a good specific capacitance of 32.1 F/g, an energy density of 11.42 Wh/kg, and 82.2% capacitance retention after 10,000 cycles, highlighting the practical potential of the MXene–polyacrylonitrile composite.

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## Electronic Materials and Photonics
## Room 207 A W - Session EM3+TF-WeA

### Materials and Devices for Advanced Photonics and Plasmonics

**Moderator: Erin Cleveland**, Laboratory of Physical Sciences

4:15pm **EM3+TF-WeA-9 Writable and Spectrally Tunable Cadmium Oxide Plasmonics via Gallium-Ion Implantation**, ***Maxwell Tolchin***[1], The Pennsylvania State University*; Bhaveshkumar Kamaliya,* McMaster University, Canada*; Angela Cleri,* The Pennsylvania State University*; Youngji Kim,* Vanderbilt University*; Morvarid Ghorbani,* McMaster University, Canada*; Anton Ievlev,* Center for Nanophase Materials Sciences, Oak Ridge National Laboratory*; Nabil Bassim,* McMaster University, Canadian Centre for Electron Microscopy, Canada*; Joshua D. Caldwell,* Vanderbilt University, Sensorium Technological Laboratories*; Jon-Paul Maria,* The Pennsylvania State University

Ion beam engineering is a promising field to advance plasmonic and nanophotonic technologies. At high (1s to 10s MeV) and low (10s to 100s keV) ion beam energies, semiconductor chemistries can be modified and constructed into spatially and spectrally coherent devices. A direct beneficiary to ion beam engineering is cadmium oxide (CdO) thin film plasmonics. High-throughput CdO thin films grown by high-power impulse magnetron sputtering (HiPIMS) have an intrinsic affinity for oxygen vacancy formation. Thereby, achieving carrier concentrations of 1.6 to 3.5 x $10^{19}$ cm$^{-3}$ while maintaining mobilities of 235 to 290 cm$^2$V$^{-1}$s$^{-1}$. By the carrier concentration to plasma frequency relation using Drude formalism, spectral ranges can span the mid-wave infrared (MWIR) spectrum. This is evident by reactively co-sputtering HiPIMS CdO with extrinsic dopants (i.e., Y, In, F) to extend carrier concentrations and mobilities to 5 x $10^{20}$ cm$^{-3}$ and 470 cm$^2$V$^{-1}$s$^{-1}$, respectively. These capabilities realize CdO as a highly programmable, low-loss material system with a chemical bandwidth to sustain high crystallinity and structural resilience. Herein, and enabled by the chemical flexibility of CdO and need for localized and wavelength-tunable plasmonics, 30 keV gallium-ion (Ga$^+$) implantation is employed. Using a focused ion beam scanning electron microscope (FIB-SEM), thermally activated Ga$^+$ implants facilitate shallow, donor-doped CdO at ion doses ranging from 1 x $10^{14}$ to 1 x $10^{16}$ ions/cm$^2$. Beam tilting techniques and iterative thermal activation conditions achieve site-specific and spectrally defined architectures. Microscopy and spectrometry support high-homogeneity Ga$^+$ distribution and characteristic morphology in CdO. Near- and far-field spectroscopy show observable changes to phonon and plasmon resonances affiliated with Ga-doping behavior. An innovative beam-stitching process affords larger pattern designs to demonstrate Hall Effect transport properties of 1.3 x $10^{20}$ cm$^{-3}$ and 372 cm$^2$V$^{-1}$s$^{-1}$. In summary, spectral tunability by Ga$^+$ implantation is on-par with optoelectronic properties seen in extrinsically doped-CdO thin films with an added dimensionality of spatially-controlled dopant writability. And, this work acknowledges the reliability of ion implantation doping for next generation plasmonics and nanophotonics by ion beam engineering.

4:30pm **EM3+TF-WeA-10 Potential-Modulated Sers Profiling via Glad-Fabricated Ag Nanorod Arrays for Ultrasensitive andLabel-Free Spectroelectrochemical Sensing**, ***Lakshay Bhardwaj***, *JP Singh,* Indian Institute of Technology Delhi, India

Routine analysis of food adulterants and pharmaceutical additives at the point of care is crucial for food safety and environmental protection. Surface-enhanced Raman spectroscopy (SERS)-based sensing has gained significant importance in various scientific and technological domains, including analytical chemistry, biomedical diagnostics, forensic science, drug discovery, environmental monitoring, and food safety. Electrochemical SERS (EC-SERS) enhances the technique by regulating surface charge, adsorption, desorption dynamics, and redox processes, improving signal intensity and selectivity. Despite having advantages, developing EC-SERS sensors for field applications remains constrained by the limited availability of robust and reproducible SERS-active electrochemical substrates. This study introduces a cutting-edge portable EC-SERS platform, leveraging silver (Ag) nanorods engineered onto screen-printed electrodes *via* a thermal evaporation-based glancing angle deposition (GLAD) technique. This innovative approach ensures exceptional signal enhancement, outstanding sensitivity, and remarkable reproducibility, making it a powerful tool for high-precision molecular detection. Potential-modulated SERS profiling of *p*-aminothiophenol, 1,2-bis-(4-pyridyl)ethylene, and melamine was carried out at various electrochemical potentials. Additionally, the maximum signal enhancement was achieved at an optimized potential (*V*max), enabling the detection of melamine with a remarkable limit of 10 pM, surpassing previously reported substrates. The results highlight the promise of GLAD-fabricated AgNRs@SPE as a sensitive, label-free, reusable, and portable EC-SERS platform. This platform will present significant improvements in detecting analytes relevant to analytical chemistry, the pharmaceutical industry, and drug control.

4:45pm **EM3+TF-WeA-11 Nano-Plasmonics for Hybrid, Far IR Photodetection: Simulation and Fabrication**, ***Basil Vanderbie***, *Samuel Fedorka, Charles Dickerson, John McElearney,* Tufts University*; Corey Shemelya,* Government*; Thomas Vandervelde,* Tufts University

Far infrared avalanche photodetectors are typically cryogenically cooled to negate thermally excited carriers from being generated in the absorption region which limits potential applications.To remove the need for cryogenic equipment a possible option is the removal of the absorption region and replacement with plasmonic nano-antennas and direct carrier injection. In this work we explore novel methods, materials, and geometries to promote direct injection and anisotropic progression of carriers into the avalanche region of a III-V PIN diode.Our proposed designs were verified by simulation with CST Microwave Studio for electromagnetics and COMSOL Multiphysics for carrier dynamics. Additionally, we have developed a unique fabrication plan for both the multi-axis junction and plasmonic resonator, as well as structures resonant in the RF regime for the purposes of a feasibility study.

5:00pm **EM3+TF-WeA-12 ML-Based Optimization of a Subwavelength Grating Polarization Filter Using Simulated and Experimental Data**, ***Patrick Flanigan***, *Manuj Mishra,* North Carolina Central University

A polarization filter is a photonic integrated circuit component that can block one type of polarization (TE or TM) while allowing the other to pass; one such example of this is a periodic (Bragg) grating with subwavelength elements. The purpose of this project is to find the conditions of the grating that will optimize the relevant figure of merit, the extinction ratio (ER), which is defined as the ratio of the passed mode transmission to the blocked mode transmission. This can be done through Monte Carlo simulations or non-linear optimization algorithms -- the method here is to sweep the available parameter space in two variables and construct a Machine Learning (ML) model to predict where the ER maximum lies within the existing data points. Both simulated and experimental data will be considered to develop the most accurate picture of the underlying physics. The simulations are based on the Finite Difference Time Domain (FDTD) method and were obtained by running the nearly-identical simulations in parallel to save time. The experimental data was obtained via the SiEPIC multi-project wafer project. In both cases, the data needs to be collected

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[1] **JVST Highlighted Talk**

for both broadband TE and TM incident light. For the ML optimization, the initial choice of algorithm will be the random forest method, due to its successful track record and suitability to the specifics of this problem.

Figure 1 shows a schematic of the system, with the key variable parameters being the grating's period (a) and tooth thickness (d); the simulations were fully three-dimensions. Figure 2 shows the simulated data that will be used for training the ML model; the experimental counterpart will be smaller in scope due to the limitations of working on a communal wafer.

## Thin Films
## Room 206 B W - Session TF1-WeA
## VSHOP V – Vapor Synthesis of Hybrid Materials and Their Properties

**Moderators: Yifan Cheng**, Virginia Tech, **Matthias Young**, University of Missouri

2:15pm **TF1-WeA-1 Hybrid Molecular Layer Deposition of Multi-Metal Alkoxide Resists for Electron Beam and Extreme Ultraviolet Lithography**, ***Long Viet Than***, *Stacey F Bent,* Stanford University

Molecular layer deposited (MLD) metal-organic photoresists have the potential to address the material challenges of extreme ultraviolet (EUV) lithography due to their advantages in thickness control and chemical homogeneity. Previous studies have utilized simple MLD schemes with a single precursor and counter-reactant pair to achieve patterning close to industrially relevant length scales. However, for further optimization, layer-by-layer deposition of multi-component films via a supercycle approach may be required to adjust properties such as sensitivity, contrast, etch resistance, mechanical strength, and others.

In this work, we explore the properties of multi-component MLD photoresists by depositing multi-metal alkoxide ('metalcone') films via both trimethylaluminum (TMA) and diethylzinc (DEZ), and ethylene glycol as the counter-reactant. Using a supercycle approach in which cycles of alucone growth (TMA and EG) are evenly distributed with cycles of zincone growth (DEZ and EG), we grow the multi-metalcone films with a range of Al/Zn ratios and characterize their properties. X-ray photoelectron spectroscopy (XPS) shows that significant transmetalation of Al and Zn occurs during deposition. However, the metal fraction can still be controlled between 40% and 95% Al (normalized against Al + Zn) by varying the fraction of alucone cycles within the supercycle between 0.25% and 50%. To assess the effect of the Al/Zn ratio on resist performance, line/space gratings with 24 nm half pitch are patterned on ~25 nm thick resist films via electron beam lithography as a proxy for EUV lithography and developed with hydrochloric acid at varying concentrations. The results show that compared to pure alucone or zincone films, the multi-metal resists have similar e-beam sensitivity (~70-100 $mC/cm^2$ depending on development conditions), but enhanced lithographic contrast (improving from a value of $\gamma = 0.38$ for alucone to a value of $\gamma = 6.3$ for the multi-metalcone) and pattern quality (reduced bridge defects and scumming). The improvements are observed even for minimal Zn incorporation in the multi-metalcone (~95% Al). From XPS studies of the resists after partial development, we attribute the improvement to the preferential dissolution of zincone from the unexposed multi-metal resist, which enhances solubility contrast. This work demonstrates the potential of supercycled MLD schemes to enable emergent interactions between components, vastly expanding the design space for this class of photoresists.

2:30pm **TF1-WeA-2 High-Throughput MLD Screening of Photoresists for EUV Lithography via UV and E-Beam Exposure**, ***Duncan Reece***, *David Bergsman,* University of Washington

As semiconductor patterning pushes toward sub-5 nm features, next-generation photoresists must deliver high resolution, environmental and chemical stability, and compatibility with extreme ultraviolet (EUV) lithography processes. However, EUV photoresist materials explored to date still face challenges such as ease of deposition and achieving sub-nanometer chemical uniformity. Molecular layer deposition (MLD) offers precise control over thin-film structure and composition, enabling the design of hybrid materials tailored to meet these challenges. Previous work has demonstrated MLD-based EUV photoresists incorporating aluminum (Al) and tin (Sn); however, the influence of the organic reactant on the final photoresist properties remains largely underexplored. Using our custom high-throughput multi-chamber MLD system, we synthesized 18 organic–inorganic hybrid films from two organometallic precursors—trimethylaluminum diethylzinc, and tetrakis(dimethylamino)tin(IV)—paired with six organic linkers: hydroquinone bis(2-hydroxyethyl) ether, 1,2,4-trihydroxybenzene, 1,5-hexadiene-3,4-diol, 2-butyne-1,4-diol, cis-2-butene-1,4-diol, and 3,4-dihydroxy-1-butene. Film candidates were screened for growth rate, ease of deposition, uniformity, and ambient stability. To assess potential photochemical reactivity, UV-induced crosslinking, or structural rearrangement, we measured thickness changes before and after solvent exposure, both with and without deep UV treatment.Selected high-performing films were subjected to electron beam lithography as a stand-in for EUV testing, followed by development to evaluate feature resolution and pattern fidelity using scanning electron microscopy and profilometry. Mechanical durability was assessed via nanoindentation, while chemical transformations were characterized with Fourier Transform Infrared Spectroscopy (FTIR) and X-ray Photoelectron Spectroscopy (XPS).Our results identify material systems that combine robust environmental and chemical resistance with promising lithographic performance and photo-reactive behavior. While EUV lithography remains the ultimate target application, e-beam serves as a high-resolution surrogate to guide photoresist development. This integrated approach demonstrates the power of high-throughput MLD and multi-parameter screening for accelerating the discovery of advanced materials for next-generation lithographic technologies.

2:45pm **TF1-WeA-3 Transforming Photo-Polymerized Organic Networks into Ceramics via Vapor Phase Infiltration (VPI)**, ***Ronan Neill***, *Li Zhang, Mark Losego,* Georgia Institute of Technology

Micropatterning of 3-dimensional structures from arbitrary ceramic materials is complicated and often expensive. In this work, we explore a new platform technology for converting an easily patterned photopolymerizable resin into a 3D ceramic structure using vapor phase infiltration (VPI) and subsequent thermal combustion.VPI is a gas-phase technique in which inorganic vapors are sorbed into a polymer, creating an organic-inorganic hybrid material.Here we are interested in studying how the chemical design of this hybrid material can affect the thermal combustion process and its conversion to a final ceramic component, without significant cracking.Ethoxylated trimethylolpropane triacrylate (ETPTA) photo-polymerizable monomers are used because they are already known to create compliant networks that readily sorb high fractions of inorganic precursors during VPI.After VPI with trimethyl aluminum (TMA) and water, the hybrid films were thermally annealed to fully combust all organics.In this talk, we will discuss how process parameters including reactor temperature and precursor exposure duration affect cracking, shrinkage, and ceramic density.In general, increased precursor loading during VPI results in reduced cracking of the alumina film, and upwards of 60% of the original film thickness could be retained after organic burnout.To assess changes in the lateral dimension micro-patterned structures were also tested, and minimal change in lateral size were detected, likely due to substrate clamping.

3:00pm **TF1-WeA-4 Measuring the Coefficient of Thermal Expansion for Vapor Phase Infiltrated Ultra-low-k Dielectric Materials for Advanced Packaging**, ***Pragna Bhaskar***, *Li Zhang, Mohanalingam Kathaperumal, Mark Losego,* Georgia Institute of Technology

Advanced interposers consist of alternate layers of copper and polymer dielectric materials. While copper has a low coefficient of thermal expansion (CTE) of 16 ppm/ $^{0}$C, ultra-low-k dielectric materials have CTEs in the range of 50-150 ppm/ $^{0}$C. This mismatch in CTE between copper and ultra-low-k dielectric materials results in lower thermomechanical reliability. Most methods available in literature involve the addition of oxide fillers to reduce the CTE of polymers. In this study, vapor phase infiltration (VPI) treatment is considered as a possible method to introduce $AlO_x$ into dry films or spin-coated and cured films. Another challenge with respect to ultra-low-k dielectric films is the measurement of CTE. Conventional CTE measurement techniques such as thermomechanical analysis (TMA) require a sample thickness of the order of few millimeters. The films in the present study have thicknesses in the range of 0.5 to 5 µm matching closely with the typical dielectric layer thickness employed in advanced packaging substrates with very high-density interconnects. Therefore, TMA cannot be used for CTE measurement of these films. Instead, temperature dependent spectroscopic ellipsometry is used to track the thermal expansion of the films and determine their CTE.These measurements demonstrate the effectiveness of the VPI process to lower the CTE of low dielectric constant polymers by about 4 to 15 times depending on the dielectric polymer, placing them near the CTE of copper.The chemical mechanisms for this lowering of the CTE will be discussed in this talk.

3:15pm **TF1-WeA-5 Machine Learning Predictions for Selecting Organic Small Molecules in Atomic Layer Processing**, ***Lucas R Kuehnel***, *Erick A Gutierrez-Monje, Anthony A Khoury, Campbell A Sweet, Matthias J Young,* University of Missouri-Columbia

Selecting organic small molecule inhibitors for area-selective atomic layer deposition and organic precursors for oxidative molecular layer deposition requires knowledge of chemical properties such as pKa, oxidation potential, physical phase, and vapor pressure. However, these data are not readily available for many candidate molecules. Machine learning using molecule-based message passing graph neural network (MPNNs) provides a strategy to establish statistical models connecting molecular structure to these physical properties using tabulated data. These models can be used to rapidly predict the properties for compounds where this data has not been measured. Here, we employ Chemprop, an established user-friendly MPNN framework, to predict chemical properties of organic small molecules relevant to atomic layer processing applications. We report on MPNN models to predict boiling point, melting point, pKa, oxidation potential, and vapor pressure given only SMILES strings as user input. At the time of submission, the mean absolute errors of baseline model predictions on unseen test data are 15.0 K for boiling point, 29.4 K for melting point, 0.749 log units for pKa, and 0.353 V for oxidation potential. The median absolute percent error is 12.5% for vapor pressure. We describe opportunities to integrate such models into semi-autonomous workflows for chemical innovation and discovery relevant to the atomic layer processing communities.

3:30pm **TF1-WeA-6 Physical Vapor Deposition of Metal Iodide Thin Films for Radiation Detections**, ***Jun Wang,*** Radiation Monitoring Devices Inc.; *Matthew Loyd,* Oak Ridge Natinal Laboratory; *Nicholas Anastasi, Lakshmi S. Pandian, Vivek V. Nagarkar,* Radiation Monitoring Devices Inc.

Metal iodides, when doped with lanthanide elements, are crucial materials in radiation detection, medical imaging, and high-energy physics applications. They belong to a class of materials called scintillators, which emit photons (fluorescence) when exposed to ionizing radiation. Metal iodide scintillators offer high light output, good energy resolution and scalability, especially in the thin film format. They can be scaled up to a few inch$^2$ or more for practical applications. However, the hygroscopic nature of these materials hinders the development and commercialization of such scintillators. At Radiation Monitoring Devices, Inc., we specialize in overcoming these challenges and developing such metal iodide scintillators through a controlled growth environment and hermetic sealing techniques. Here we present the development of a well-known lithium iodide (LiI) scintillator, in a large micro-columnar thin film of up to 4 inch$^2$ in size via a physical vapor deposition in a special integrated glovebox system. The developed LiI film doped with europium (Eu) scintillator boasts a remarkable ultra-high brightness of approximately 22 times that of GS20 (commercially available screens), while the cerium (Ce) doped LiI film offers an ultra-fast decay time of 50 ns. Both films offer a high spatial resolution, excellent gamma-neutron discrimination and high detection efficiency for advanced thermal neutron imaging applications, which are especially suitable for integration with special neutron detectors in national neutron facilities such as Spallation Neutron Source (SNS) and High Flux Isotope Reactor (HFIR) at Oak Ridge National Laboratory. We report recent advancements in the fabrication and characterization of such next-generation LiI scintillator films for thermal neutron imaging applications.

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## Thin Films
## Room 206 B W - Session TF2-WeA

### Fundamentals of Thin Films II

**Moderator: Qihua Zhang**, Pennsylvania State University

4:15pm **TF2-WeA-9 Flipping the Switch on Tin Sulfide Deposition: From SnS to SnS$_2$**, *Christopher Brewer, Hy Nguyen, Reed Woolard,* ***Amy Walker,*** University of Texas at Dallas

Tin sulfides ($Sn_xS_y$ ) are non-toxic and inexpensive materials with low band gaps, making them suitable for semiconductor applications and photovoltaic materials, such as solar cells. $Sn_xS_y$ has three naturally occurring compositions, SnS, $Sn_2S_3$, and $SnS_2$. The ability to control the stoichiometry of a $Sn_xS_y$ deposit is of interest for devices like SnS solar cells, where $Sn_2S_3$ contamination reduces the device efficiency. Tin disulfide is an emerging 2D layered metal dichalcogenide which has applications in electronics and as a photodetector. In this study we investigate the selective deposition of tin sulfides using chemical bath deposition (CBD) on organic substrates. We employ alkanethiolate self-assembled monolayers (SAMs) functionalized with $-CH_3$, -OH, and -COOH terminal groups as model organic substrates. Our data shows that the substrate functionality does not strongly influence the composition of the deposit. Rather, the tin sulfide deposition can be flipped from SnS to $SnS_2$ by changing tuning the bath pH. Under basic conditions using tin(II) chloride and thioacetamide, pure SnS is deposited at pH ≥ 11. The data also suggests that the functional group of the SAM directs the phase of the SnS deposited, providing potentially an easier route to the newly discovered cubic SnS phase. In contrast, under acidic conditions $SnS_2$ is deposited using tin(II) choloride and tartaric acid as a complexing agent. The deposition results will be discussed in the context of our mechanism based approach to tune the bath chemistry to achieve composition control of the $Sn_xS_y$ deposit.

4:30pm **TF2-WeA-10 Homoepitaxial Growth of ZrB2 on a ZrB2(0001) Surface**, *Michael Trenary,* ***Ayoyele Ologun,*** University of Illinois - Chicago

Zirconium diboride ($ZrB_2$), a group-IV metal-terminated diboride, is an extremely hard material with a high melting point of 3246 °C. Thin films of $ZrB_2$ can be grown conformally via chemical vapor deposition (CVD) using zirconium borohydride, $Zr(BH_4)_4$, as a precursor. Homoepitaxial growth of $ZrB_2$ was studied using scanning tunnelling microscopy (STM). Exposure of $Zr(BH_4)_4$ to the $ZrB_2(0001)$ surface at 1400 K led to the formation of $ZrB_2$ islands. Coarsening of the $ZrB_2$ islands into layers via Smoluchowski ripening was observed when the islands were left for 60 minutes at 1400 K before imaging at room temperature. In contrast, exposure at 900 K resulted in high-density clusters. Stepwise annealing at 1400 K led to the transformation of these clusters into a continuous thin film via thermal-induced coalescence, with moiré patterns observed as intermediate structures during this coalescence process.

4:45pm **TF2-WeA-11 Multilayered Films for High Hardness**, ***Nestor Marquez Rios,*** *Nathaniel McIlwaine, Jon-Paul Maria,* The Pennsylvania State University

Multilayered high entropy carbide films were synthesized by physical vapor deposition (PVD) using bipolar high-power impulse magnetron sputtering (HiPIMS) with methane gas as the carbon source. Shutter automation and asynchronous plasma were used to alternate between two HiPIMS cathodes, enabling modulation of the metal composition leading to superlattice structure formation. The resulting structure consists of two rock salt structured solid solution layers forming a periodic multilayer. Crystallinity was characterized by Xray diffraction (XRD), which demonstrated the ability to grow multilayer sequences with modulated periods ranging from 3 nm to 50 nm, engineered to reach a total film thickness of 1.5 µm changes in the position of low and high order satellite peaks were observed confirming a multilayer period consistent with the designed bilayer thickness. Surface morphology and topography were characterized using scanning electron microscopy (SEM) and atomic force microscopy (AFM). Mechanical properties were evaluated using Knoop and Vickers microindentation techniques to determine the influence of nanoscale engineering by making multilayer on hardness.

5:00pm **TF2-WeA-12 Hot Complex Oxides – Unlocking New Materials and New Physics via High Temperature Adsorption Controlled Molecular Beam Epitaxy** , ***Brendan Faeth,*** Epiray; *Matt Barone, Tobias Schwaigert, Anna Park, Vivek Anil, Dylan Sotir, Yorick Birkholzer, Kyle Shen, Darrell Schlom,* Cornell University

It has long been understood that molecular-beam epitaxy works best for materials that can be grown in an adsorption-controlled regime where thermodynamics automatically provides composition control.This approach has found greatest success for GaAs and other compound semiconductors, fundamentally underlying the capability of MBE to produce semiconductor films with the highest reported purity and mobilities. To date, however, adsorption control processes in complex oxide materials have been limited to specific systems, as the majority of binary oxide constituent compounds (SrO, BrO) remain non-volatile up to ~1000 °C, the typical limit for conventional MBE substrate heater technologies.Here, we utilize a powerful $CO_2$ laser for MBE substrate heating, allowing access to growth temperatures up to and beyond 2000 °C on virtually all commercially available oxide substrates.Utilizing this approach, we have grown an increasing number of complex oxides in unconventional, ultra-high temperature adsorption-controlled regimes by MBE, some realized here for the first time in epitaxial thin film form.In each case we observe substantial improvements in structural and electronic properties as characterized by transport, XRD, and/or in situ angle-resolved photoemission spectroscopy measurements.In this talk, we outline the technical basis and future possibilities for $CO_2$ laser heating in MBE, specifically discussing recent results for SrTiO3, BaTiO3, SrMoO3, and Sr2MoO4 grown at substrate temperatures in the 1200-1500 °C range.

5:15pm **TF2-WeA-13 Machine-Learned Relationships between Particle Flux, Kinetic Energy, and Experimental Conditions in Pulsed Laser Deposition***, Zahra Nasiri, Dorien Carpenter, Jacob H Paiste,* University of Alabama at Birmingham*; Sumner B Harris,* Oak Ridge National Laboratory, USA*; **Renato P Camata**,* University of Alabama at Birmingham

In pulsed laser deposition (PLD), the kinetics of crystal growth is strongly dependent on the flux (Φ) and the kinetic energy (*K*) of plume species arriving at the substrate. These factors vary widely with target materials and deposition conditions. While scaling laws and prior experience provide some guidance, quantitatively predicting the dependence of Φ and *K* on the laser fluence (*F*) and spot area (*A*) is challenging. Even in well-established PLD laboratories, it is typical for only limited regions of the functions Φ(*F*, *A*) and *K*(*F*, *A*) to be known for specific materials and laser wavelengths. Moreover, these regions often shift due to target surface evolution and subtle experimental variations, demanding time-consuming and costly re-optimization experiments.

Machine learning (ML) algorithms can process PLD plume diagnostic data in real time and generate high-quality dynamic models of Φ(*F*, *A*) and *K*(*F*, *A*). These can be integrated into decision-making workflows to control experimental actuation, either to maintain or deliberately adjust thin film growth conditions according to specified protocols.

In this work we show how high-fidelity representations of Φ(*F*, *A*) and *K*(*F*, *A*) can be generated by Gaussian Process Bayesian Optimization (GPBO) from a small number of experiments. A Gaussian process regression model is trained on progressively accumulating data to produce surrogate models of the objective functions Φ(*F*, *A*) and *K*(*F*, *A*). We compare active learning workflows using different acquisition functions and GP kernels with random sampling. We evaluate the process using synthetic PLD data generated by laser ablation-fluid dynamics simulations. The model produces physically plausible Φ(*F*, *A*) and *K*(*F*, *A*) for specific PLD conditions and target materials. Typical results for PLD of copper (Cu) with $F$ = 1–10 J/cm$^2$ and $A$ = 0.8–13 mm$^2$—obtained from 1000 model runs starting with random 3-point seed pairs of (*F*, *A*)—show that our GPBO process can discover optimum flux and kinetic energy conditions after as few as three iterations (i.e., experiments) using the probability of improvement (PI) acquisition function. Finally, we will show how introducing a physics-informed, structured mean in the Gaussian process—based on the well-known scaling behavior of Φ and *K* with vapor density (proportional to *F*) and Mach number of the expansion (proportional to *A*)—affects the performance of the GPBO.

## 2D Materials
## Room 208 W - Session 2D+AQS+EM+MI+MN+NS+QS+SS+TF-ThM

### 2D Materials: Optoelectronics and Moire Excitons

**Moderator: Daniel Yimam**, Oak Ridge National Laboratory

8:00am **2D+AQS+EM+MI+MN+NS+QS+SS+TF-ThM-1 Probing the Ultrafast Charge Dynamics and Exciton Emission from Single Atomic Defects in 2D Semiconductors by Lightwave-Driven STM***, Laric Bobzien, Lysander Huberich, Jonas Allerbeck, Eve Ammerman, Nils Krane, Andres Ortega-Guerrero, Carlo Pignedoli, Oliver Gröning,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland*; Joshua A. Robinson,* The Pennsylvania State University*; **Bruno Schuler,*** Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland **INVITED**

Two-dimensional (2D) semiconductors provide an exciting platform to engineer atomic quantum systems in a robust, yet tunable solid-state system. This talk explores the intriguing physics of single point defects in transition metal dichalcogenide (TMD) monolayers, investigated through atomically resolved scanning probe microscopy.

We have determined the layer-dependent charge transfer lifetimes of selenium vacancies in $WSe_2$ on graphene substrates, spanning picosecond to nanosecond timescales [1]. By leveraging our recently developed lightwave-driven scanning tunneling microscope (THz-STM) [2,3], we could probe the ultrafast charge dynamics on the atomic scale. Time-domain sampling with a THz pump-THz probe scheme enabled capturing atomic-scale snapshots of transient Coulomb blockade, a hallmark of charge transport mediated by quantized defect states [4].

Moreover, the extended charge state lifetimes provided by hBN decoupling layers facilitated the local, electrical stimulation of excitonic emission from pristine $MoS_2$ and individual charged defects via STM luminescence (STML).

By combining the structural and electronic properties accessible by conventional scanning probe microscopy with the optical fingerprint from STML and the excited-state dynamics revealed through pump-probe THz-STM, we gain a comprehensive microscopic understanding of localized quantum states in low-dimensional materials.

References:
[1]L. Bobzien et al. Phys. Rev. Lett. (accepted, arxiv: 2407.04508)
[2]J. Allerbeck et al. ACS Photonics 10, 3888 (2023)
[3]L. Bobzien et al. APL Mater. 12, 051110 (2024)
[4]J. Allerbeck et al. arXiv:2412.13718 (2024)
[5]L. Huberich et al. (in preparation)

8:30am **2D+AQS+EM+MI+MN+NS+QS+SS+TF-ThM-3 Many-Body Effects on Excitons, Trions, and Defect-Bound States in 2D Materials***, **Kai Xiao,** Taegwan Park, Alexander Puretzky,* Oak Ridge National Laboratory, USA*; Xufan Li,* Honda Research Institute*; Kyungnam Kang,* Oak Ridge National Laboratory, USA*; Austin Houston,* University of Tennessee, Knoxville*; Christopher Rouleau, David Geohegan,* Oak Ridge National Laboratory, USA

Two-dimensional (2D) materials, particularly transition metal dichalcogenides (TMDs) exhibit strong many-body interactions due to reduced dielectric screening and spatial confinement. These interactions, involving electrons, holes, excitons, phonons, and plasmons, give rise to emergent phenomena distinct from their bulk counterparts. In this talk, I will present our recent investigations into the many-body effects on the optical properties and ultrafast excitonic dynamics of monolayer and bilayer TMDs. Specifically, we synthesized isotopically pure monolayer $MoS_2$ and highly defective $WS_2$ via nonequilibrium chemical vapor deposition, enabling a controlled study of isotope effects, defects, and background doping on excitonic behavior. Using ultrafast laser spectroscopy and temperature-dependent optical spectroscopy, we observed pronounced many-body interactions, including exciton-phonon and exciton-electron coupling, which significantly influence exciton energy, dynamics, and light-matter interactions in both monolayer and bilayer TMDs. These strong interactions give rise to novel quantum states and make 2D materials promising platforms for next-generation optoelectronics, quantum information technologies, and fundamental condensed matter physics.

Synthesis science was supported by the U.S. Dept. of Energy, Office of Science, Materials Science and Engineering Division. This work was performed at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.

8:45am **2D+AQS+EM+MI+MN+NS+QS+SS+TF-ThM-4 Proximity-Induced "Magic" Raman Bands in TERS Spectra of MoS2 / WS2 @ 1L H-BN-Capped Gold***, **Andrey Krayev,*** HORIBA Scientific*; Pavel Valencia Acuna,* PNNL*; Ju-Hyun Jung,* Pohang University of Science and Technology (POSTECH), Republic of Korea*; Cheol-Joo Kim,* POSTECH, Republic of Korea*; Andrew Mannix,* Stanford University*; Eleonora Isotta,* Max Planck Institute for Sustainable Materials, Germany*; Chih-Feng Wang,* PNNL

Recently it was proposed to use the monolayer h-BN – capped gold substrates as an ideal platform for the gap mode TERS and TEPL imaging, that on the one hand, should preserve strong gap mode enhancement of Raman signal due to small thickness (0.3 nm) of the dielectric h-BN layer, and on the other hand preserve strong TEPL response due to de-coupling of 2D semiconductors from the metallic substrate. TERS data collected on mono- and a few-layer-thick crystals of $MoS_2$ and $WS_2$ on 1L-h-BN-capped gold show both the TERS and TEPL response, confirming the validity of the proposed approach.

In addition to the enhancement of both the PL and Raman signal, in the course of assessment of TERS/TEPL response of mono- and a few-layer-thick crystals of $MoS_2$ and $WS_2$ deposited on 1L h-BN-capped gold we observed in TERS spectra, completely unexpectedly, appearance of Raman bands at about 796 $cm^{-1}$ and 76 $cm^{-1}$ which are not normally observed in regular Raman spectra of h-BN or $WS_2$/$MoS_2$. We can safely state that these "magic" bands belong to h-BN as they appear at the same spectral position in TERS spectra of both the monolayer $MoS_2$ and $WS_2$ deposited on the monolayer h-BN capped gold, moreover, the 796 $cm^{-1}$ band often was the strongest band observed in TERS spectra, even stronger than A' mode from $WS_2$ or $MoS_2$. Presence of the transition metal dichalcogenide (TMD) monolayer is mandatory for the appearance of these "magic" bands as they are absent outside of the monolayer TMDs in these samples. Literature search showed that similar (but not identical) phenomenon was observed earlier in h-BN encapsulated $WSe_2$,$MoSe_2$, and $WS_2$. There have been several significant differences between our data and the earlier reported one: in our case we have not been able to observe the "magic bands" in $MoSe_2$ and $WSe_2$ @ 1L h-BN@Au, while $WS_2$ monolayers deposited on the same substrate as $WSe_2$, showed expected response. More importantly, the excitation laser wavelength dependence in our case was completely different from what was reported earlier: in $WS_2$-based samples we observed strong "magic" bands with excitation at 830 nm, 785nm, 594nm, but not 633nm, the wavelength closest to the A exciton in this material. This excitation profile is remarkably reminiscent of the excitation profile of the monolayer $WS_2$ in intimate contact with silver where we observed strong dip of the intensity of main A' mode in TERS spectra at 633nm excitation wavelength.

We will argue that intricate interaction between the tip-substrate gap plasmon, TMD excitons and most probably, normally mid-IR-active phonons in h-BN is responsible for the appearance of observed "magic" bands.

9:00am **2D+AQS+EM+MI+MN+NS+QS+SS+TF-ThM-5 Correlated Excitons in TMDC Moiré Superlattice***, **Sufei Shi,*** Carnegie Mellon University **INVITED**

In a strongly correlated electronic system, Coulomb interactions among electrons dominate over kinetic energy. Recently, two-dimensional (2D) moiré superlattices of van der Waals materials have emerged as a promising platform to study correlated physics and exotic quantum phases in 2D. In transition metal dichalcogenides (TMDCs) based moiré superlattices, the combination of large effective mass and strong moiré coupling renders the easier formation of flat bands and stronger electronic correlation, compared with graphene moiré superlattices. Meanwhile, the strong Coulomb interaction in 2D also leads to tightly bound excitons with large binding energy in TMDCs. In this talk, we will discuss how to use optical spectroscopy to investigate excitonic physics and strongly correlated phenomena in TMDC moiré superlattice, along with correlated exciton states arising from strong interactions.

9:30am **2D+AQS+EM+MI+MN+NS+QS+SS+TF-ThM-7 Sub-Stoichiometric Phases in 2D $MoTe_2$***, **Onyedikachi Alanwoko**, Nirosha Rajapakse, Matthias Batzill,* University of South Florida

Atom vacancy formation in crystalline materials is energetically expensive. To lower the energy cost for non-stoichiometry, point defects can condense into energetically more favorable extended defects. Studies on Mo-dichalcogenides have shown that excess Mo is condensed into closed, triangular Mirror Twin Boundary (MTB) loops. These MTBs can form in high densities where the triangular loops connect and form a cross-hatched network of MTBs. Here we show through Scanning Tunneling Microscopy (STM) that periodically ordered MTB networks can obtain a homologous series of sub-stoichiometric $MoTe_{2-x}$ phases. We systematically investigate the preparation conditions (which include a variation of the growth temperature, Te-desorption by post-growth annealing, and vapor-deposited Mo), enabling the controlled synthesis of these new phases. The different phases require different synthesis procedures, and once formed, these phases appear thermally stable in vacuum. The ability to control and create these different phases of $MoTe_2$ and other two-dimensional (2D) materials is a promising way of realizing new electronic and chemical properties of 2D materials. Particularly promising is the observation that we can react $MoTe_2$ with dissimilar transition metals to create new doped or alloyed 2D materials with potentially desirable properties.

11:00am **2D+AQS+EM+MI+MN+NS+QS+SS+TF-ThM-13 Microwave Imaging of Excitonic States and Fractional Chern Insulators in 2D Transition Metal Dichalcogenides***, **Zhurun Ji**,* SLAC National Accelerator Laboratory/ MIT **INVITED**

Nanoscale electrodynamics offers a unique perspective on states with bulk-edge correspondence or spatially dependent excitations. I will introduce our latest advancements in optically coupled microwave impedance microscopy, a technique that enhances our capability to explore electrodynamics at the nanometer scale. I will discuss our recent studies utilizing this technology to extract spectroscopic information on exciton excitations within transition metal dichalcogenide systems. Additionally, I will share our recent findings on probing topological and correlated electronic states, specifically the fractional Chern insulator states in twisted TMD bilayers.

11:30am **2D+AQS+EM+MI+MN+NS+QS+SS+TF-ThM-15 Control and Properties of Single Dislocations in Van Der Waals Nanowires***, **Peter Sutter**, Eli Sutter,* University of Nebraska - Lincoln

Line defects (dislocations) not only govern the mechanical properties of crystalline solids but they can also produce distinct electronic, thermal, and topological effects. Identifying and accessing this functionality requires control over the placement and geometry of single dislocations embedded in a small host volume to maximize emerging effects. We have identified a synthetic route that enables the rational placement and tuning of dislocation in van der Waals nanowires, where the 2D/layered crystal structure limits the possible defect configurations and the nanowire architecture puts single dislocations in close proximity to the entire host volume.[1] While homogeneous layered nanowires carry individual screw dislocations, the synthesis of radial (core-shell) nanowire heterostructures transforms the defect into a mixed (helical) dislocation whose edge-to-screw ratio is continuously tunable via the core–shell lattice mismatch.

Such deterministic control over defects now enables the probing of functionality arising with single dislocations. For example, germanium sulfide van der Waals nanowires carrying single screw dislocations incorporate Eshelby twist and thus adopt a chiral twisted structure,[2] which for the first time allowed the identification of chirality effects in the photonic properties of a single nanostructure.[3] Using cathodoluminescence spectroscopy, whispering gallery modes could be excited and probed to directly compare the photonics of chiral and achiral segments in single nanowires. The data show systematic shifts in energy, which with the help of simulations are assigned to chiral whispering gallery modes in wires hosting a single dislocation.

The ability to design nanomaterials containing individual dislocations with controlled geometry paves the way for identifying a broad range of functional properties of dislocations, with the potential to herald a paradigm shift from the traditional strategy of suppressing dislocations to embracing and harnessing them as core elements of new technologies.

1. P. Sutter, R.R. Unocic, and E. Sutter, *Journal of the American Chemical Society* 145, 20503 (2023); DOI: 10.1021/jacs.3c06469
2. P. Sutter, S. Wimer, and E. Sutter, *Nature* 570, 354 (2019); DOI: 10.1038/s41586-019-1147-x
3. P. Sutter, L. Khosravi-Khorashad, C.V. Ciobanu, and E. Sutter, *Materials Horizons* 10, 3830 (2023); DOI: 10.1039/D3MH00693J

11:45am **2D+AQS+EM+MI+MN+NS+QS+SS+TF-ThM-16 Two-Dimensional Keldysh Theory for Non-Resonant Strong-Field Ionization of Monolayer 2D Materials***, **Tsing-Hua Her**,* UNC Charlotte*; Che-Hao Chang,* NTHU, Taiwan*; Kenan Darden,* UNC Charlotte*; Tsun-Hsu Chang,* NTHU, Taiwan*; Hsin-Yu Yao,* NCCU, Taiwan

Over the past decade, a diverse array of intense light interactions with monolayer two-dimensional (2D) materials have been reported, including low- and high-order harmonic generation (HHG), multiphoton absorption, optical injection of spin and charge currents, terahertz generation, and laser-induced dielectric breakdown. These processes are all initiated by interband transition of electrons induced by light with photon energy smaller than the bandgap energy. Some modeling efforts based on perturbation theory were attempted but their discrepancies with experiments are at least one order of magnitude, highlighting the lack of theoretical understanding of strong-field ionization in monolayer 2D materials. In this work, we report a new formalism of strong-field ionization for monolayer two-dimensional semiconductors based on 2D Keldysh (KLD) theory [T. -H. Her et al., Optica 12, 538-545 (2025)]. We take this approach because the original Keldysh theory [L. V. Keldysh, Soviet Physics JETP **20**, 8 (1965)] is the only theory that yields, for simplified band dispersion, analytical formulas for the cycle-averaged non-resonant ionization rate in bulk solids induced by a monochromatic electric field of arbitrary strength. It provides a smooth transition between multiphoton and tunneling ionization as what we now call the 'Keldysh parameter', , varies from >>1 to <<1. Due to their analyticity, Keldysh's formulas are widely employed for qualitative modeling of strong-field ionization in bulk solids. In this presentation, we generalize Keldysh's formulas to monolayer two-dimensional semiconductors. We derive closed-form formulas and their asymptotic forms for a two-band model with a Kane dispersion. We also derive selection rules related to the parity of multiphoton orders near the band edge. We validate our theory by comparing it to recent experiments and modeling of strong-field ionization in monolayer transition metal dichalcogenides (TMDs) with very good agreement (Figs. 1-3 of supplemental document) Specifically, our theory predicts a higher interband electron tunneling rate for 2D compared to 3D in the MIR frequency range, which successfully explains the 10x discrepancy (Fig. 3) between the experiment and modeling for HHG from monolayer TMDs [Liu et al., Nature Phys 13, 262–265 (2017)]. Considering the tremendous success of the original Keldysh theory in describing strong-field optical phenomena in atoms and solids, our 2D Keldysh theory is expected to find a wide range of applications in intense light-2D material interaction, such as optical limiting, multi-photon photodetection, THz generation through quantum interference, and photo-carrier doping for HHG.

12:00pm **2D+AQS+EM+MI+MN+NS+QS+SS+TF-ThM-17 Thickness Dependent Band Gap and Electrical Anisotropy of 2DSnSe***, Marshall Frye, Jonathan Chin, Joshua Wahl, Jeremy Knight,* Georgia Institute of Technology*; Walter Smith,* Purdue University*; Dilara Sen, Samuel Kovach,* Kenyon University*; Frank Peiris,* Kenyon College*; Charles Paillard,* University of Arkansas*; Thomas Beechem,* Purdue University*; Anna Osterholm, **Lauren Garten**,* Georgia Institute of Technology

2D SnSe presents unique opportunities for optoelectronics, and scalable microelectronics, but it is first critical to understand how the electrical and optical response change upon downscaling. Tailoring the band gap and electrical anisotropy of 2D monochalcogenides, like SnSe, has previously been shown but the mechanisms that drive the changes in band gap are still not understood. This study revealshow changes in bond length and structure drive the thickness dependences of band gap, carrier mobility and lifetime of SnSe thin films.Molecular beam epitaxy is used to deposit (2h00) oriented SnSe thin films with thicknesses ranging from 4 nm to 80 nm. The direct band gap increases from 1.4 eV at 80 nm to 1.9 eV at 4 nm, underscoring the potential of SnSe as a tunable and direct band gap material for thin film optoelectronics. Raman spectroscopy showsdifferent simultaneously changes in the crystal structure and bonding occurring parallel versus perpendicular to the 2D plane with decreasing film thickness. TEM further supports the hypothesis that the increase in the band gap with reduced thickness is due to changes in crystal structure resulting in a contraction of the out-of-plane SnSe covalent bonds, while the in-plane bond length increases. In addition to the reduction in band gap, tracking the time dependent photoluminescence shows an increase in carrier lifetime with decreasing film thickness, while Hall measurements show a change in the carrier mobility with decreasing thickness. Overall, this work provides the critical missing insight needed to design these optically and electronically relevant2D materials for scalability.

## Atomic Scale Processing Mini-Symposium
## Room 206 A W - Session AP+AS+EL+EM+PS+TF-ThM

### Advancing Atomic Scale Processing through Modeling and Simulation

**Moderator: Sagar Udyavara**, Lam Research Corp

8:00am **AP+AS+EL+EM+PS+TF-ThM-1 Multiscale Simulations for Atomic Scale Processing*, Michael Nolan,*** Tyndall Institute, Ireland **INVITED**

In modern semiconductor device fabrication, the dimensions involved require atomic level control over materials deposition and etch. Atomic Level Processing, exemplified by Atomic Layer Deposition (ALD) and thermal atomic layer etch (tALE), is therefore critical deposition and etch of relevant materials. Further scaling and use of complex three-dimensional structures means that Thermal ALE will take centre stage in etching. The key chemistry takes place at surfaces which drives the self-limiting characteristics and other advantages of these atomic level processing approaches. In this presentationt I will discuss how atomistic simulations based on first principles Density Functional Theory, ab initio Molecular Dynamics and kinetic Monte Carlo methods can be used to predict the chemistry of atomic level deposition and etch processes. I will first discuss the key chemistries involved in atomic level processing chemistries and the challenges that we have identified in this exciting area.The first scientific topic is the simulation of plasma enhanced deposition (PE-ALD) of metals, using the example of cobalt for next generation interconnects. This is the first example of an atomistic level study of the full PE-ALD cycle for Co metal and show that the process requires use of ammonia or mixed H2/N2 plasma. Calculated energy barriers for key steps give guidance regarding the temperatures required for the process. We show how substrate pre-treatment can reduce nucleation delay and therefore allow selectivity in deposition of the target film. Finally we show how kinetic Monte Carlo can be used to predict the structure of deposited metal films on different nitride substrates using data from DFT level simulations.The second example is molecular layer deposition of hybrid materials, using alucone as the prototypical example. Comparison of aliphatic with functionalized aromatic molecules allows differences in film properties to be understood. A further application of this involves selective, templated deposition of target films using block co-polymer infiltration where differences in reactivity of a precursor in two polymers promotes selective deposition of the target films. Finally, I present our work on self-limiting thermal atomic layer etching (ALE), highlighting how simulations can (1) predict the window of self-limiting etch (2) unravel the difference between amorphous and crystalline substrates and (3) probe the impact of surface orientation on tALE chemistry, all of which are important for future, selective thermal ALE processing on complex 3D substrates.

8:30am **AP+AS+EL+EM+PS+TF-ThM-3 The Si-Cl2-Ar+ Atomic Layer Etching Window: Fundamental Insights from Molecular Dynamics Simulations and a Reduced Order Model*, Joseph Vella*[1]*,*** TEL Technology Center, America, LLC, USA*; David Graves,* Department of Chemical and Biological Engineering Princeton University

Plasma assisted atomic-layer etching (ALE) processes are frequently characterized by the ALE window. This is a range of ion energies where the amount of substrate etched remains constant as a function of the ion energy. Silicon (Si) etch by alternating exposure to chlorine gas (Cl$_2$) and argon ions (Ar$^+$) is frequently used as a demonstrative example to illustrate concepts of ALE, including the ALE window.[1] Despite this, when examining the literature, properties of the ALE window for this system remain obscure. For example, Kim et al.[2] studied Si-Cl$_2$-Ar$^+$ ALE and report that the ALE window should be below 40 eV. On the other hand, Park et al.[3] report the ALE window as being from 70 to 90 eV. Still others report an Ar$^+$ ion energy of 50 eV as being within the ALE window.[4] In this talk, we aim to resolve these contradictory reports by studying the Si-Cl$_2$-Ar$^+$ ALE with classical molecular dynamics (MD) simulations and a reduced order model (ROM).[5] The MD results show that the range of Ar$^+$ ion energies where the amount of Si etched per cycle (EPC) remains relatively constant is from 15eV to 20 eV, which is very narrow. The EPC in this region is also less than one atomic layer, because atomic Cl sputtering is significant. The results also show that a large ion fluence (roughly 4.2 $10^{16}$ ions/cm$^2$ for 15 eV ions) is required to remove all Cl from the near surface region, which is a key insight when developing processes that achieve “true ALE”. Using the ROM, parameters can be varied to observe their effect on properties of the ALE window. For example, by increasing the threshold sputtering energy of Si, the width of ALE window can be increased. While this study focuses on the relatively simple Si-Cl$_2$-Ar$^+$ system, it is clear learnings from this study can be extended to other systems.

**References**

[1] T. Lill, “Atomic Layer Processing: Semiconductor Dry Etching Technology” (Wiley-VCH, Weinheim, 2021).

[2] B. Kim, S. Chung, and S. M. Cho, “Layer-by-later Etching of Cl-adsorbed Silicon Surfaces by Low Energy Ar$^+$ Ion Irradiation”, Appl. Surf. Sci. 2002, 187, 124-129.

[3] S. Park, K. Min, B. Yoon, D. Lee, and G. Yeom, “Precise Depth Control of Silicon Etching using Chlorine Atomic Layer Etching” Jpn. J. Appl. Phys. 2005, 44, 389-393.

[4] K. J. Kanarik, T. Lill, E. A. Hudson, S. Sriraman, S. Tan, J. Marks, V. Vahedi, and R. A. Gottscho, “Overview of Atomic Layer Etching in the Semiconductor Industry”, J. Vac. Sci. Technol. A, 2015, 33, 020802.

[5] J. R. Vella, Q. Hao, M. A. I. Elgarhy, V. M. Donnelly, and D. B. Graves, “A Transient Site Balance Model for Atomic Layer Etching”, Plasma Sources Sci. Technol., 2024, 33, 075009.

8:45am **AP+AS+EL+EM+PS+TF-ThM-4 Influence of Fluorination and Oxygenation Sources on the Thermal Atomic Layer Etching of MoS2*, Spencer Smith,*** *Jacob A. Tenorio, Icelene Leong, John D. Hues, Steven M. Hues, Elton Graugnard,* Boise State University

Atomic layer etching (ALE) has emerged as a pivotal technique in the precise fabrication of two-dimensional (2D) materials, particularly molybdenum disulfide (MoS$_2$), which holds promise in the semiconductor industry due to its high mobility in monolayer form. The ability to precisely etch amorphous and crystalline MoS$_2$ films provides a pathway for controlling thickness, which is critical to achieving desired electrical and optical properties. Previous studies used MoF$_6$ and H$_2$O in thermal ALE of MoS$_2$. Here, we report studies of alternate sources of fluorination and oxygenation and evaluate their impact on thermal ALE of MoS$_2$. Oxygen sources include water and ozone, and fluorine sources include HF/Pyridine and MoF$_6$. Etch rates, uniformity, and surface chemistry post ALE were characterized using spectroscopic ellipsometry, atomic force microscopy, and X-ray photoelectron spectroscopy. Results indicated at ALE of amorphous MoS$_2$ with HF with either H$_2$O or O$_3$ showed no signs of etching at 200 ºC or 250 ºC. Whereas the combination of MoF$_6$ + O$_3$ at 250 ºC on amorphous MoS$_2$ films exhibited an etch rate of 1.6 Å/cycle and a mass loss of 44 ng/cm$^2$. Further MoF$_6$ + O$_3$ etching at 200 ºC showed a mass loss of 19 ng/cm$^2$, similar to prior reports using MoF$_6$ + H$_2$O at 200 ºC. Surface morphology showed little change from etching, but surface oxygen concentration increased. This research further expands the capabilities for atomic layer processing of 2D materials.

9:00am **AP+AS+EL+EM+PS+TF-ThM-5 Insights Into Atomic Layer Etching of Diamond Surfaces*, Jack Draney*,** *Athanassios Panagiotopoulos, David Graves,* Princeton University

Thanks to its nitrogen vacancy color centers, diamond is a candidate for many quantum applications from quantum sensing to quantum computing. Pristine surfaces engineered for each application are required for good device performance. We investigated atomic-scale plasma processing as a method for reaching these pristine diamond surfaces. Our investigation takes the form of combined experiments and molecular dynamics simulations, allowing atomic-scale insights into the effects of argon / oxygen atomic layer etching on diamond surfaces.

9:15am **AP+AS+EL+EM+PS+TF-ThM-6 Benchmarking Large Language Models for Atomic Layer Deposition*, Angel Yanguas-Gil,*** *Matthew T. Dearing, Jeffrey W. Elam, Jessica C. Jones, Sungjoon Kim, Adnan Mohammad, Chi Thang Nguyen, Bratin Sengupta,* Argonne National Laboratory

In this work we introduce an open-ended question benchmark, ALDbench, to evaluate the performance of large language models (LLMs) in the field of atomic layer deposition. Our benchmark comprises questions with a level of difficulty ranging from graduate level to domain expert current with the state of the art in the field. Human experts reviewed the questions along the criteria of difficulty and specificity, and the model responses along four different criteria: overall quality, specificity, relevance, and accuracy. We ran this benchmark on an instance of OpenAI's GPT-4o using an API interface. This allows us to fine tune hyperparameters used by the LLM for text generation in a way that is not possible using conventional chat-based interfaces.

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[1] **JVST Highlighted Talk**

The responses from the model received a composite quality score of 3.7 on a 1 to 5 scale, consistent with a passing grade. However, 36% of the questions received at least one below average score. An in-depth analysis of the responses identified at least five instances of suspected hallucination. We also observed statistically significant correlations between the following question and response evaluation criteria: difficulty of the question and quality of the response, difficulty of the question and relevance of the response, and specificity of the question and the accuracy of the response. Finally, we will address other issues such as reproducibility, impact of hyperparameters on the quality of the response, and possible ways in which the performance of the LLMs can be further improved.

[1] A. Yanguas-Gil et al, J. Vac. Sci. Technol. A 43, 032406 (2025)

9:30am **AP+AS+EL+EM+PS+TF-ThM-7 Developing a "Digital Twin" for Area-Selective Deposition on 3D Nanopatterns***, **Nicholas Carroll**, Gregory Parsons,* North Carolina State University

Area-selective deposition (ASD)—a bottom-up patterning technique that enables precise material deposition on specific regions while preventing deposition elsewhere—has garnered significant attention as an augmentation to lithographic patterning of nanoscale features during semiconductor manufacturing. Some potential applications, such as contact-over-active-gate, will require multiple ASD materials to be deposited in sequence, heightening the challenge of effective process design. Given the vast time and resources required for experimental assessments of process integration, demand is rapidly growing for a "digital twin" (i.e. a software representation of a physical system) of device fabrication sequences. A comprehensive ASD digital twin will require advances in analyzing atomic layer deposition (ALD) reactor design and mechanistic insights into interactions between inhibitor molecules, ALD reactants, and substrate surfaces over time as reactions proceed.

We have recently developed a stochastic lattice model describing metal oxide ASD on planar substrates, including means to visualize the film shape and extent of lateral overgrowth during ASD.[1] Parameters in the model can be adjusted based on steric hindrance during each half-cycle, differences in interfacial energies between the non-growth surface and the growing film, and the preferred molecular bonding orientations. These factors elucidate subtleties in shape evolution during ASD, but results to date have been limited to vertical and lateral growth on 2D surfaces. A functional ASD digital twin must describe ASD on arbitrary 3D nanopatterns and on sub-lithographic feature sizes, including effects of selectivity loss where the selectivity decreases as film thickness increases.

We will present recent efforts in our group to extend the functionality of the stochastic lattice model to describe ASD on 3D substrates, including surfaces with pattern dimensions less than 10 nm. On very small features, for example, the model shows that lateral growth during ASD results in a wide distribution of feature separation distances, even when the growth per cycle is uniform across a growing film surface. We will also discuss intricacies that need to be considered to integrate multiple ASD steps into processes involving more complex "multi-color" substrates where several substrate materials exposed to reactants simultaneously. We believe that such insight will be critical for the realization of a functional digital twin model of atomic-scale processing needed for future semiconductor devices and other advanced manufacturing processes.

(1) Carroll, N. M.; Parsons, G. N. *J. Vac. Sci. Technol. A* **42** (6), 062411 (2024).

9:45am **AP+AS+EL+EM+PS+TF-ThM-8 Activation of C-X Bonds on Transition Metal Surfaces: Insight from DFT Studies***, **Matias Picuntureo,*** Universidad Tecnica Federico Santa Maria, Chile*; Ilker Tezsevin, Marc Merkx,* Eindhoven University of Technology, The Netherlands*; Scott Semproni, Jiun-Ruey Chen,* Intel Corporation*; Adriaan Mackus,* Eindhoven University of Technology, The Netherlands*; Tania Sandoval,* Universidad Tecnica Federico Santa Maria, Chile

Area-selective atomic layer deposition (AS-ALD) represents an advanced bottom-up nanofabrication technique enabling selective material growth on targeted areas of patterned substrates. In advanced semiconductor manufacturing, such as next-generation processes at the back end of line (BEOL), small molecule inhibitors (SMIs) can enable AS-ALD through the selective formation of inhibitor layers on metal surfaces that block deposition.

A recent study by Merkx et al. reported hydrogenolysis and potentially dehydrogenation of aniline on Ru surfaces during AS-ALD, leading to the formation of a carbonaceous layer with enhanced inhibition performance. This highlights the importance of understanding the driving forces behind the surface chemistry of SMIs.

To explore whether similar surface-mediated reactions can occur for other inhibitor–metal combinations, we employ density functional theory (DFT) to investigate the adsorption and dissociation mechanisms of benzene-derived SMIs on Ru(0001), Mo(110), and W(110) surfaces.

To enable a systematic comparison across different molecules and surfaces, our study focuses on radical-mediated dissociation pathways involving the cleavage of functional groups from the aromatic ring. This approach allows us to isolate the effect of the functional group and its interaction with the metal surface in determining the reaction thermodynamics between the molecular and dissociated adsorbed states.

We find that charge transfer to the adsorbed inhibitor modulates its dissociation energy landscape. The resulting radical intermediates are substantially stabilized through coordination with the metal surface. We further explore their subsequent hydrogenation, which transforms these surface-bound radicals into more stable, saturated species. Lastly, we show that the fate of reaction by-products—whether they remain adsorbed or desorb into the gas phase—can significantly impact the overall reaction thermodynamics and shift the equilibrium toward or away from product formation.

The investigation of the reaction pathways explored in this study contributes to the fundamental understanding of molecule–surface interactions during AS-ALD and offers insight that may support future strategies for the rational design of small molecule inhibitors.

References:

[1] Merkx et al., J. Chem. Phys. 160, 2024.

11:00am **AP+AS+EL+EM+PS+TF-ThM-13 Descriptor-driven analysis of inhibitors for AS-ALD processes***, Joost F. W. Maas, Marc J. M. Merkx,* Eindhoven University of Technology, Netherlands*; Matías Picuntureo, Lucas Lodeiro,* Universidad Tecnica Federico Santa Maria, Chile*; Adriaan J. M. Mackus,* Eindhoven University of Technology, Netherlands*; **Tania E. Sandoval**[1,2],* Universidad Tecnica Federico Santa Maria, Chile

Area selective atomic layer deposition (AS-ALD) is a bottom-up technique that can address some of the challenges that limit the nanofabrication of complex structures, which require patterning and alignment at the atomic scale. Currently, one of the most robust strategies to carry out AS-ALD is with the use of small molecule inhibitors (SMIs), that selectively adsorb and inhibit the non-growth surface (NGS) and prevent precursor adsorption. These SMIs range from a variety of functionalities and structures depending on the target NGS, and their selection is based on specific criteria, such as reactivity, volatility, and safety.[1,2]

Currently, the library of tested inhibitor molecules is very limited, therefore finding the best candidate for a given surface is challenging. Using computational tools can significantly accelerate the expansion of this library through high-throughput screening and recent advances in machine learning. In the case of the use of descriptors,[3] the goal is to correlate the performance of the SMIs e.g., measured in terms of their stability, as adsorption energy, with the dependence on materials or molecular properties. The derived correlations can serve to establish general guidelines for SMI selection, expanding the analysis to other molecules not included in the initial study. This approach has proven to be very successful in reducing computational costs in other fields, such as heterogeneous catalysis and drug discovery.

In this presentation, we provide an overview of the dependency between a list of descriptors and the adsorption energies of SMIs candidates on a variety of relevant NGS, such as oxides, nitrides, and metals. We explore descriptors based on the molecular properties, such as electronegativity, electrophilicity, and orbital energy, as well as descriptors based on the electronic structure of the material, such as d-band center. Results indicate a with strong correlation with the adsorption energy ($E_{ads}$) and electronegativity of the core-atom on the adsorption of oxides and nitrides, as well as the d-band center on the adsorption on metal surfaces. Moreover, our data highlights the differences in reactivity across surfaces and the challenges in surface passivation across surfaces with similar surface sites. Overall, this study provides important insights into the use of descriptor-driven analysis in the selection of the right SMI candidates for the advancement of ASD processes.

[1] A. Mameli and A. Teplyakov *Acc. Chem. Res.* 2023, 56, 2084−2095.

[2] P. Yu, et al. *Appl. Surf. Sci.* 2024, 665, 160141.

[3] C. Chen, et al. *J. Phys. Chem. C* 2025, 129, 13, 6245–6253.

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[1] **TFD Paul Holloway Award Winner**

[2] **JVST Highlighted Talk**

11:15am **AP+AS+EL+EM+PS+TF-ThM-14 Understanding Plasma-Induced Bonding and Composition Changes in SiCN ALD via kMC–DFT Modeling***, **Ting-Ya Wang,*** University of Texas at Austin*; Hu Li, Peter Ventzek,* Tokyo Electron America*; Gyeong Hwang,* University of Texas at Austin*; Jianping Zhao,* Tokyo Electron America

Plasma-enhanced atomic layer deposition (PEALD) enables low-temperature processing of silicon carbonitride (SiCN), a critical low-k material for advanced interconnects. However, energetic plasma species—including both ions and radicals—can significantly influence surface reactions, film composition, and structural evolution, ultimately affecting material properties such as dielectric constant and mechanical strength. A comprehensive understanding of these species-specific effects is essential for process optimization.

Integrating kinetic Monte Carlo (kMC) with density functional theory (DFT) offers a powerful approach for simulating ALD. However, a key challenge in kMC lies in the need for a predefined list of permissible events. Traditionally, researchers manually compile a set of reactions deemed most significant. Yet, the vast number of possible events on a surface, combined with the importance of rare events in ALD, raises concerns about the authenticity and completeness of outcomes derived from manually curated reaction lists.

To address this, we developed an atomistic, off-lattice, three-dimensional simulator that integrates kMC with DFT. We employed a strategic approach to construct a comprehensive event list, capturing a broad spectrum of potential surface reactions. This year, we expand our study in four key directions: (1) comparison of ion- and radical-driven reaction pathways to delineate their distinct roles in modifying surface chemistry; (2) evaluation of different plasma chemistries (e.g., $N_2$ vs. $NH_3$) to understand how reactive species impact film stoichiometry and termination; (3) simulation of multi-cycle growth to track the evolution of defects and compositional shifts; and (4) simulation predictions against experimental data such as XPS and IR spectra.

Our findings reveal a synergistic interplay between ions and radicals in shaping the formation of Si–N, Si–C, and C–N bonding networks. The simulation platform enables insights into plasma–surface interactions, offering a predictive framework for optimizing SiCN PEALD processes.

11:30am **AP+AS+EL+EM+PS+TF-ThM-15 Understanding SiCN Film Oxidation Mechanism Through Density Functional Theory***, **Tsung-Hsuan Yang**, Hu Li, Jianping Zhao, Peter Ventzek,* Tokyo Electron America

Low dielectric constant (low-k) spacers are essential components in advanced microelectronic devices for mitigating parasitic capacitance and crosstalk, leading to enhanced device performance. Among low-k materials, silicon carbon nitride (SiCN) is widely used for its tunability in dielectric constant, leakage current and chemical robustness. However, the long-term stability of SiCN films is often compromised by atmospheric moisture, leading to the formation of silicon oxide. To address this issue, we utilize density functional theory (DFT) to elucidate the fundamental oxidation mechanisms of SiN and SiC components by $H_2O$. Reaction rates were estimated with a combination of transition state theory and Arrhenius equation, enabling prediction of oxidation rates under various processing conditions. Additionally, $H_2O$ diffusion within SiCN films was modeled, demonstrating a direct correlation between film density and oxidation kinetics. More importantly, the findings in this work can be applied in depositing SiOCN film as the oxidation mechanisms are predicted to be similar with other oxidation agents. Knowledge of these oxidation mechanisms enables precise control of the SiOCN film deposition process, facilitating component tunability.

11:45am **AP+AS+EL+EM+PS+TF-ThM-16 From Bulk Titanium Nitride to Small Molecule Inhibitors: a DFT Study Aiming Towards Area-Selective Atomic Layer Deposition***, **Lucas Lodeiro,*** Universidad Tecnica Federico Santa Maria, Chile*; Marc J. M. Merkx,* Eindhoven University of Technology, The Netherlands*; Dennis M. Hausmann, Rachel A. Nye de Castro,* LAM Research*; Adriaan J. M. Mackus,* Eindhoven University of Technology, The Netherlands*; Tania E. Sandoval,* Universidad Tecnica Federico Santa Maria, Chile

Titanium Nitride (TiN) is a hard and inert ceramic used as a protective coating, and in microelectronics for its metallic behavior. TiN thin films improve devices performance as conductive connection and diffusion barrier, and can be further functionalized to promote specific applications. Atomic Layer Deposition (ALD) enables precise TiN film deposition, with temperature controlling crystal growth facet. However, achieving area-selective ALD (AS-ALD) on TiN is challenging, because the lack of information of surface groups present in deposited TiN, requiring reliable surface models to search for solutions for precursor selectivity and inhibition with Small Molecule Inhibitors (SMIs) at atomic scale.

This study uses Density Functional Theory (DFT) to examine TiN surface properties, crystal facets, and surface chemistry. It also explores the adsorption of various organic and inorganic precursor (Al, Si, Ti-based) and SMI (aryl, aldehyde, and nitrogen-based) molecules on TiN with the aim of studying their potential for AS-ALD processes with TiN as growth or non-growth area.

Our findings on crystal facets align with experimental data, showing the (001) facet is the most stable, followed by the (111) facet, which is observed at high deposition temperature.[1] The reactivity and functionalization strategies of these surfaces differ significantly. The (001) surface shows low reactivity (especially with $H_2O$, $NH_3$, and $H_2$), resulting in bare surface sites.[2] Conversely, the (111) surface is reactive and can undergo hydrogenation, altering its electronic properties.

The differences in electronic surface properties significantly affect surface chemistry and the adsorption mechanism of the different molecules. The (001) surface exhibits metallic behavior, with strong interactions with various functional groups (for example, -1.8 eV for Benzaldehyde, BA), similar to copper surfaces.[3] In contrast, adsorption on the (111) surface is weaker and mainly dispersive (-0.8 eV for BA), highlighting the importance of the TiN film facet. Experimental findings show enhanced inhibition of BA and higher selectivity for low temperature deposited TiN, which could indicate the presence of the (001) surface, and a more stable inhibitor adsorption.

The key findings of this study offer valuable insights into surface reactivity and electronic properties to use TiN in AS-ALD process. Ultimately, this work aims to provide insights into controlling TiN deposition at the nanoscale, opening avenues for advanced microfabrication and surface engineering applications.

[1] Met. Mater. Int. 2001, 7, 621–625.

[2] J. Phys. Chem. C 2013, 117, 38, 19442–19453.

[3] Chem. Mater. 2025, 37, 1, 139–152.

12:00pm **AP+AS+EL+EM+PS+TF-ThM-17 Trimethylaluminum Reactivity on $SiO_2$ Surfaces at Cryogenic Temperatures – Implications for $Al_2O_3$ ALD***, **Leonhard Winter**, Ravi Ranjan, Francisco Zaera,* University of California, Riverside

The atomic layer deposition (ALD) of aluminum oxide films on solid substrates using trimethylaluminum (TMA) and water is often considered a prototypical ALD process. Several investigations have attempted to understand the mechanistic details of this deposition by following the corresponding steps *in situ* under reaction conditions. To gain a more fundamental understanding, we have set out to study this system following a UHV surface-science approach, slowing down the reaction, decreasing the gas exposures and substrate temperature, and following the progress of the reactions using surface science techniques. We chose to study this chemistry on $SiO_2$ films grown *in situ* onto a Ta support because $SiO_2$ is one of the most common substrates in the microelectronics industry.

We investigated the adsorption and reaction of TMA with $SiO_2$ by using X-ray photoelectron spectroscopy (XPS) and temperature-programmed desorption (TPD). We found that TMA starts to react with the $SiO_2$ surface at ≈110 K, i.e. below the cryogenic temperatures required for multilayer condensation. This low-temperature chemistry appears to be complex, as multiple reaction pathways can be deduced from analysis of the TPD data. In addition to the expected product methane, we observed the formation of ethylene and heavier fragments, probably also containing Al. The complex behavior of TMA on $SiO_2$ is not limited to low temperatures, as the loss of alkyl groups continues over several hundred kelvins upon heating of the sample. Isothermal adsorption experiments show that at room temperature the TMA uptake is self-limiting with an initial sticking coefficient that is approximately 4-5 times smaller than at cryogenic temperatures, where multilayer growth occurs. To model ALD-type growth, we alternately dosed TMA and water at 200 K and followed the chemical composition of the surface with XPS. The results are in agreement with the expected ALD behavior, which shows that ALD growth is possible at these extremely low temperatures for the TMA/water system. The two precursors were also co-dosed in a CVD-type deposition, which results in the growth of multilayer films of aluminum oxide on the $SiO_2$ substrate. Surprisingly, the growth was observed to proceed faster at 200 K than at room temperature, which we explain by a kinetic effect of prolonged residence times of the precursors at lower surface temperatures.

## Thin Films
## Room 206 B W - Session TF+CPS+MS+EM-ThM
### Thin Films for Microelectronics I

**Moderators: Elton Graugnard**, Boise State University, **Robert Grubbs**, IMEC Belgium

8:00am **TF+CPS+MS+EM-ThM-1 Pushing the Limits of Vertical NAND Storage Technology with ALD-based Ferroelectrics**, *Prasanna Venkatesan,* Georgia Institute of Technology*;* ***Asif Khan,*** Georgia Institute of Technology, USA **INVITED**

Solid-state drives (SSDs) continue to serve as the foundation of long-term active data storage in modern data centers. Over the past decade, conventional vertical NAND (vNAND) technology has achieved a remarkable 50× increase in storage density, enabled by advances in physical scaling (x–y and z dimensions) and logic scaling (from multi-level cell, MLC, to quad-level cell, QLC). The explosive growth of artificial intelligence (AI)—with models like GPT-4 surpassing a trillion parameters—has further accelerated the demand for high-capacity, high-performance storage systems to support petabyte-scale datasets.

Today's state-of-the-art vertical NAND devices offer densities nearing 30 Gb/mm$^2$ with over 300 stacked layers. However, extending this scaling trajectory to 1000 layers and beyond—targeting storage densities exceeding 100 Gb/mm$^2$—poses significant challenges. Chief among these are reliability concerns intrinsic to charge-trap flash technologies, such as lateral charge migration and the poor endurance of higher logic level operations.

To overcome these limitations, ferroelectric field-effect transistors (FeFETs) have emerged as a promising alternative, enabling further z-direction scaling with improved reliability. This presentation will highlight recent advances in atomic layer deposition (ALD)-based ferroelectric gate stack engineering, and how these innovations can support the development of next-generation NAND architectures capable of 1000-layer integration and ultra-high-density storage.

8:30am **TF+CPS+MS+EM-ThM-3 Electrical Properties of BaTiO3 Thin Films Prepared by Atomic Layer Deposition**, ***Jiayi Chen,*** *Asif Khan, Mark Losego,* Georgia Institute of Technology

This talk will discuss our efforts to develop a robust atomic layer deposition process (ALD) to create ferroelectric $BaTiO_3$ thin films. Ferroelectric materials are potential candidates for future low voltage RAM and NAND memory because of their reversible two polarization states under low external electric field. While the CMOS compatible gate dielectric materials $HfO_2$ and $Hf_{0.5}Zr_{0.5}O_2$ are ferroelectric, they have high coercive fields that make it difficult to lower switching voltages below 1 V. Therefore, perovskite ferroelectric materials, like $BaTiO_3$ are desirable to use for these applications because their coercive voltages can be an order of magnitude lower, approaching 0.1 V. However, these ferroelectric films must be deposited by ALD to match the conformality and small thickness requirements desired for RAM and NAND memory. This talk will present the electrical properties of $BaTiO_3$ thin films deposited by an ALD process using Bis-(1,2,4 triisopropylcyclopentadienyl)-Barium and Titanium Isopropoxide precursors. We are able to achieve dielectric constants as high as 15 in as-grown (non-crystalline) thin films, and 140 in annealed (crystalline) thin films, with low leakage current ($10^{-4}$ A / cm$^2$ at 3 V). Specifically, we will focus on the variations of dielectric constant and leakage current as we optimize deposition recipe, $BaTiO_3$ thin films' stoichiometry, scale down the thickness from 50 nm to 10 nm, and measure at cryogenic and elevated temperatures. We will also discuss the implications of these measurements, and the possible route to achieve ferroelectric $BaTiO_3$ thin films by ALD.

8:45am **TF+CPS+MS+EM-ThM-4 Interlayer-Modulated Coercive Field in $HfZrO_2$ Ferroelectric Devices**, ***Marshall Frye***[1,2]*, John Wellington-Johnson, Lance Fernandes, Prasanna Ravindran, Asif Khan, Lauren Garten,* Georgia Institute of Technology

Ferroelectric NAND (FeNAND) using $Hf_{0.5}Zr_{0.5}O_2$ (HZO) offers increased memory density, speed, and decreased operation voltage of NAND compared to charge trap flash technology.[1] However, to compete with charge trap flash, the memory window of FeNAND must be increased above 6 V for 3 bit/cell operation or above 8 V to enable 4 bit/cell operation.[1] Since the memory window is directly related the ferroelectric coercive field ($E_c$), finding pathways to increase the coercive field of HZO is critical to enable FeNAND. Prior studies show that inserting a dielectric interlayer can increase the coercive field, but the mechanism driving the increase in $E_c$ beyond just adding a capacitor in series is still unclear.[2]

The goal of this work is to test the hypothesis that the increased defect states in the dielectric-HZO interface cause in-built fields that then increase the coercive field.[3] First, we fabricate 19 nm HZO both with and without $Al_2O_3$interlayers or adjacent layers. Varying the layer thicknesses and positions via atomic layer deposition allows for the determination of how the device structure impacts the ferroelectric switching. Polarization-electric field hysteresis loops and positive-up-negative-down (PUND) show ferroelectric switching for each of the films, with a remnant polarization ($2P_r$) up to 27.4 μC/cm$^2$. The coercive field increases from 1.01 MV/cm in devices without an additional dielectric layer (19 nm HZO) to 3.11 MV/cm in a 3 nm $Al_2O_3$ interlayer inserted between two 8 nm layers of HZO (8 nm HZO-3 nm $Al_2O_3$-8 nm HZO). First-order reversal curve (FORC) analysis reveals an increase in internal bias field in devices with dielectric layers, potentially due to defects at the $Al_2O_3$ - HZO interface. X-ray photoelectron spectroscopy valence band measurements confirm an increase in mid-gap defect states at this interface compared to bulk of the film. Additionally, temperature-dependent modulus spectroscopy is used to evaluate the activation energy and defect concentration in samples with and without a dielectric layer. These findings provide key insights into mechanisms to modulate coercive field in HZO, enabling the design of FeNAND devices with larger memory windows.

References

[1] G. Kim et al., *J. Mater. Chem. C* **2022**

[2] L. Fernandes et al., *IEEE Trans. Electron Devices* **2025**

[3] D. Das et al., *Int. Electron Devices Meet. IEDM*, **2023**

9:00am **TF+CPS+MS+EM-ThM-5 Towards Low-Resistance p-Type Contacts to 2D Transition Metal Dichalcogenides Using Plasma-Enhanced Atomic Layer Deposition**, ***Ageeth Bol,*** University of Michigan, Ann Arbor **INVITED**

One major limitation of 2D transition metal dichalcogenide (TMD) based FETs is the high contact resistance between metallic electrodes and semiconducting channels, particularly for p-type contacts. In this presentation I will address how PEALD of p-type TMDs can be used to improve this contact resistance. First, I will go over controlled doping strategies to form p-type 2D TMD contact materials using PEALD, with an emphasis on Nb Doped $WS_2$. Our recent results show contact resistancevalues as low as 0.30 ± 0.26 kΩ·μm between Pd and PEALD NbxW1-xS2, demonstrating that low resistance contacts between metal and p-type TMDs are possible. Then, I will discuss reducing unintentional p-doping introduced during PEALD of TMDs. PEALD TMDs typically contain some level of hydrogen impurities that leads to unintentional p-doping. We have shown that these impurities can be reduced by introducing an Ar plasma C step in the standard PEALD TMD process. Finally, the use of remote plasmas in PEALD for contact deposition can lead to the creation of undesired impurities and defects in the 2D TMD channel, possibly impacting electronic behavior. I will present some first insights into the defects that are created during PEALD on 2DTMDs and how we can reduce the number of plasma-induced impurities and defects.

9:30am **TF+CPS+MS+EM-ThM-7 Self-Limiting Atomic Layer Deposition of Few-Layer $MoS_2$**, ***Sungjoon Kim,*** *Jeffrey Elam,* Argonne National Laboratory

Computational energy consumption has been increasing exponentially, making energy-efficient microelectronics and computing an urgent need. Three-dimensional integrated circuits (3D ICs) and neuromorphic computing promise to revolutionize information technology by drastically reducing the energy consumption of computers, and two-dimensional (2D) semiconductors like molybdenum disulfide ($MoS_2$) can enable such technologies. However, scalable and controllable manufacturing processes are still needed to realize the technology's full potential. Here, we demonstrate the uniform and controlled deposition of few-layered $MoS_2$ using atomic layer deposition (ALD) for the purposes of memtransistor fabrication. By leveraging the equilibrium shift from material deposition to material etching, a self-limiting deposition of $MoS_2$ is achieved where material growth is stopped after the initial few layers. The resulting few layer $MoS_2$ was characterized using Raman spectroscopy and X-ray photoelectron spectroscopy, and was used to fabricate and test memtransistors. This deposition strategy is straightforward, robust and more scalable compared to other methods such as powder CVD and exfoliation.

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

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

9:45am **TF+CPS+MS+EM-ThM-8 DOE's Energy Efficiency Scaling for Two Decades (EES2): Featuring ALD-Fabricated Microelectronics Devices for Ultra-Energy-Efficient Computation at Argonne National Laboratory***, **Emilie Lozier,*** U.S. Department of Energy, Advanced Manufacturing Office*; Jeffrey Elam,* Argonne National Laboratory*; Desiree Salazar,* Energetics*; Tina Kaarsberg,* U.S. Department of Energy, Advanced Manufacturing Office

Electricity demand in the U.S. is projected to grow ~2% annually, potentially reaching a 50% increase compared to today by 2050 (International Energy Agency 2025). A major driver of this growth is the rise of energy-intensive AI computation, according to a bottom-up analysis of data center energy use published by Lawrence Berkeley National Laboratory (LBNL) in December 2024. Including cryptocurrency mining, LBNL's report projects that data-center-based computation could account for roughly a quarter of total U.S. electricity consumption by 2028. While efforts are underway to increase generation to the grid, any solution must simultaneously address the energy efficiency of compute if it is to be successful. Kicking off three years ago, the U.S. Department of Energy (DOE) Advanced Materials and Manufacturing Technologies Office (AMMTO) has already been leading a multi-organization effort united around the shared aim of advancing ultra-energy-efficient compute technologies. This collaborative effort, known as the Energy Efficiency Scaling for Two Decades (EES2) initiative, is uniquely situated to take on this energy challenge. Through EES2, DOE/AMMTO has convened eight working groups representing more than 70 voluntarily pledging organizations across industry, academia, nonprofits and the National Labs to draft an R&D Roadmap describing technologies-to-beat to achieve biennial energy efficiency doubling for the compute stack compounding to a 1,000X efficiency increase by 2040. Moreover, Version 1.0 of the R&D Roadmap (available here: https://eere-exchange.energy.gov/FileContent.aspx?FileID=f4234e29-cc0c-4a56-a510-86b616ab5535) has spurred a suite of EES2-identified and DOE-funded research projects to pursue some of the most promising technologies for enabling ultra-energy-efficient computation. This presentation will highlight one such project at Argonne National Laboratory – with collaborators at Stanford University, Northwestern University, and Boise State University – that has been advancing two-dimensional semiconductor field-effect transistors (2D-FETs) and memtransistors, both fabricated with atomic layer deposited (ALD) molybdenum sulfide ($MoS_2$) with potential to achieve 50X and 10,000X energy efficiency improvements, respectively. Along with timely project updates, this presentation will also discuss how the Argonne project will integrate with the finalized Version 1.0 of the EES2 R&D Roadmap, that is due to be published in the second half of 2025.

11:00am **TF+CPS+MS+EM-ThM-13 Integrated Magnetoacoustic Isolator with Giant Non-Reciprocity***, Bin Luo, Benyamin Davaji,* ***Nian-Xiang Sun,*** Department of Electrical and Computer Engineering, Northeastern University **INVITED**

Recent advances in integrated nonreciprocal components—such as isolators and circulators—have enabled transformative wireless communication and sensing technologies, including full-duplex radio, in-band self-interference cancellation, and protected high-power transmission systems. While commercial ferrite-based isolators offer low insertion loss and high power handling, their reliance on kOe-level bias fields, high-temperature ferrite growth, and bulky permanent magnets severely limits their compatibility with CMOS processes and low-power applications.

To address these limitations, magnetoacoustic isolators have emerged as a promising class of passive, CMOS-compatible, and power-efficient nonreciprocal devices. These isolators consist of magnetic heterostructures integrated within the propagation path of surface acoustic waves (SAWs) on piezoelectric substrates. Magnetoelastic and magnetorotational coupling mechanisms enable strong spin wave–acoustic wave interactions, generating hybrid magnetoacoustic waves with dramatically asymmetric damping rates in opposite directions. This asymmetry yields unidirectional transmission, fundamental to nonreciprocal operation.

Despite progress, early devices suffered from weak non-reciprocity, primarily due to a mere helicity mismatch effect and an inherent symmetric spin wave dispersive relation in single-layer magnetic films. Recent efforts have focused on engineering magnetic stacks with nonreciprocal spin wave dispersion. Key examples include: (i) **interfacial Dzyaloshinskii–Moriya interaction (iDMI) stacks** like CoFeB/Pt, (ii) **interlayer dipolar-coupled (IDC) stacks** such as FeGaB/$SiO_2$/FeGaB, and (iii) **RKKY synthetic antiferromagnets** like CoFeB/Ru/CoFeB. These architectures achieve nonreciprocity strengths up to 250 dB/mm. Recent demonstrations using shear-horizontal waves in $LiTaO_3$ substrates coupled to ferromagnetic and anti-magnetostrictive bilayers have yielded nonreciprocity levels of 60–82 dB/mm with simpler fabrication.

Nevertheless, a persistent challenge remains in reducing insertion loss while maintaining wide bandwidth and high isolation. We will introduce our recent efforts in a **fundamental mode SAW-driven** magnetoacoustic isolator with **giant non-reciprocity** and a **wideband nonreciprocal** magnetoacoustic isolator based on **non-collinear dipolar-coupled ferromagnetic stacks**. The talk will provide a comprehensive overview of the mechanisms, material platforms, and experimental breakthroughs driving the field of magnetoacoustic isolators. We will highlight the path toward integrated, low-loss, and high-performance nonreciprocal components for future quantum, RF, and IoT systems.

11:30am **TF+CPS+MS+EM-ThM-15 Stress Control and Thermal Stability of a FeCo-Ag Multilayer Thin Films for Use in Magnetoelectric Heterostructures***,* ***Thomas Mion****, Konrad Bussmann,* US Naval Research Laboratory

This investigation studies the stress control and thermal properties of FeCo/Ag multilayer thin films prepared by sputter deposition for their potential applications in magnetoelectric heterostructure devices. While development of magnetoelectric devices has increased, the practical implementation of magnetic thin films is often confounded by additional processing and packaging steps which can be detrimental to the quality of the magnetic film and subsequently the performance of the device. We show the annealing of the FeCo/Ag multilayers is robust until annealing temperatures reach 300 – 400 C where a breakdown of the Ag leads to an increased coercive field, and annealing >400 C is severely detrimental to the soft magnetism of the system as the Ag layers deteriorate. Additionally, as-deposited stress can play a dominant role in micromechanical devices when released. We will show the stress control of this ferromagnetic thin film through in-situ substrate bias allows the films to be tailored from a broad range of +320 MPa tensile to -300 MPa compressive with application of up to a -120 VDC bias during deposition.

11:45am **TF+CPS+MS+EM-ThM-16 Extraordinary Magnetoresistance in High-Mobility $SrTiO_3$ Thin Films***,* ***Zhifei Yang***[1]*, Shivasheesh Varshney,* University of Minnesota*; Sreejith Sasi Kumar, Tristan Steegemans, Rasmus Bjørk, Dennis Valbjørn Christensen,* Technical University of Denmark*; Bharat Jalan,* University of Minnesota

Magnetoresistive sensors are widely used to detect magnetic fields by measuring changes in electrical resistance. One such effect, extraordinary magnetoresistance (EMR), arises from the geometry of semiconductor-metal hybrid structures that combine high-mobility semiconductors with highly conductive metals. EMR strongly depends on both the semiconductor's mobility and the quality of the metal-semiconductor contact (ohmic contact with low contact resistance). The device geometry further influences boundary conditions and current paths under magnetic fields, enabling flexible design and performance tuning. While most previous EMR studies have focused on III-V semiconductors and 2D materials, there has been limited exploration of oxide-based systems.

Here, we demonstrate EMR in high-quality La-doped $SrTiO_3$ thin films grown on $SrTiO_3$ (001) substrates using hybrid molecular beam epitaxy (MBE). We grow films with carrier concentrations ranging from $\sim 2\times10^{17}$ cm$^{-3}$ to $\sim 1\times10^{20}$ cm$^{-3}$, achieving Hall mobilities from ~300 cm$^2$/(V·s) up to over 50,000 cm$^2$/(V·s) at 1.8 K. Using an asymmetric device geometry that breaks mirror symmetry between voltage probes, we observe corresponding asymmetry in magnetoresistance (MR) measurements. With embedded metals that are ohmic contacts to $SrTiO_3$, we achieve an MR $((R(B) - R(0))/R(0)$, where $R(B)$ is the measured resistance at magnetic field B) approaching 9000% at 9 T and 1.8 K, which is over 3900% higher than the intrinsic MR of $SrTiO_3$ – a *world record* for an oxide-based EMR device! Finite element simulations of current flow and MR in these $SrTiO_3$-based hybrid structures align well with experimental data, validating the design principles. These results establish the potential of complex oxide systems for low-temperature EMR sensors and open opportunities for integrating oxide heterostructures in future magnetoelectronic devices. In this presentation, we will discuss the hybrid MBE growth and microfabrication of high-mobility $SrTiO_3$ thin films, along with device optimization strategies and detailed magnetotransport measurements across various temperature and magnetic field ranges.

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[1] **AVS Graduate Research Awardee**

12:00pm **TF+CPS+MS+EM-ThM-17 Examining the Spin Structure of Altermagnet MnTe Epilayers Grown by Molecular Beam Epitaxy**, ***Qihua Zhang***[1], The Pennsylvania State University; *Mingyu Yu,* University of Delaware; *Alexander Grutter, Christopher Jenson, William Ratcliff, Julie Brochers,* National Institute for Science and Technology (NIST); *Narendirakumar Narayanan, Thomas Heitmann,* University of Missouri; *Nitin Samarth, Stephanie Law,* The Pennsylvania State University

As a new class of magnetic materials, altermagnets feature alternating arrangement of magnetic moments with zero net magnetization, a typical characteristic of an antiferromagnet; yet they also feature large spin splitting in its electronic band structure. NiAs-phase (α-) MnTe has gained significant attention as a candidate of altermagnet family owing to its large spin-splitting energy and high transition temperature. In this study, we investigate the altermagnet properties of MBE-grown α-MnTe layers using neutron diffraction experiments. We first study and optimize the growth conditions of MnTe layers grown directly on InP (111)A substrates. It is seen that using a lower growth temperature result in a narrower full-width-at-half-maximum (FWHM) in the x-ray diffraction (XRD) rocking curves, but will introduce whiskers on the surface, while increasing the Te/Mn flux ratio improves both the crystalline quality and the surface morphology. With a temperature window of 250-400 °C and a Te/Mn flux ratio of 3, we further obtain high quality α-MnTe films with a 0.8 nm surface roughness and a corresponding threading dislocation density of ~$7.5\times10^{8}$ $cm^{-2}$. Temperature-dependent neutron diffraction measurements were performed on the MnTe films grown with optimized conditions. A fitted Néel temperature of 304 K was obtained based on the half-order antiferromagnetic peak along the (0001) direction, which confirmed the bulk-like antiferromagnetic behavior in the α-MnTe. Using polarized neutron reflectometry, substantial spin asymmetry is captured while very small net magnetization (up to 4 emu/$cm^3$) across the MnTe layer is obtained, highlighting a near-to-ideal stoichiometric α-MnTe. Angle-resolved photoemission spectroscopy is further used to confirm the spin splitting in the eletronic band structure. This study carefully clarifies the magnetic band structure in a promising altermagnet candidate and introduces potential methods of controlling the ferromagnetism in the materials.

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[1] **TFD Distinguished Technologist Award**

## 2D Materials
## Room 208 W - Session 2D+AQS+MI+NS+QS+TF-ThA

### 2D Materials: Magnets and Topological Phenomena
**Moderators: Rafik Addou**, The University of Texas at Dallas, **Zhurun Ji**, MIT

2:15pm **2D+AQS+MI+NS+QS+TF-ThA-1 Non-Local Transport from Magnetic Topological Superconductivity in 2D Fe-Chalcogenides*, Kenneth Burch,*** Boston College **INVITED**

Magneto-Chiral topological superconductivity is a rare phase long pursued for error-free quantum computation. Its 1D chiral modes possess topologically protected long-range coherence well beyond that of the cooper pairs, which could be fruitful for quantum transduction and low-temperature spin transport. While evidence for such modes is mounting, unambiguous signatures, such as non-local transport via co-tunneling, remain elusive. I will describe our realization of 1D chiral hinge modes mediating the direct tunneling of electrons from source to drain in FeTe0.55Se0.45. Specifically, I will discuss our evidence that the non-local tunneling signatures are decoherence-free and emerge from this material's combination of surface magnetism, bulk topology, and superconductivity. Time remaining, I will discuss how these advances can be used for Majorana Circuits and future efforts in cryogenic spintronics

2:45pm **2D+AQS+MI+NS+QS+TF-ThA-3 Integer and Fractional Chern insulators in moiré $MoTe_2$*, Yihang Zeng,*** Purdue University **INVITED**

The fractional Chern insulator (FCI), a lattice analogue of the renowned fractional quantum Hall state, was theorized to exist without external magnetic field. FCI provides a pathway towards novel topologically ordered quantum phases that are useful for decoherence-free quantum computation. Two-dimensional (2D) moiré materials, featuring strong correlation, non-trivial band topology and unparalleled tunability, stands as an ideal platform for realizing FCI. In this talk, I will first present our innovative optoelectronic detection method, which is capable of detecting the chemical potential in arbitrary 2D materials. Employing this new technique, we successfully observed an FCI and integer Chern insulator in the zero magnetic field limit in $MoTe_2$-based moiré materials. We further study the FCI and ferromagnetism as a function of twist angle.

3:15pm **2D+AQS+MI+NS+QS+TF-ThA-5 Conducting Scanned Probe Investigations of the Bismuthine Termination of Intrinsic Topological Superlattice $Bi_2$-$Bi_2Se_3$***, Lakshan Don Manuwelge Don, Mysidia Leff, Md. Sakauat Hasan Sakib,* Miami University*; Seth Shields,* The Ohio State University*; **Joseph Corbett**,* Miami University

Topological materials, characterized by symmetry-protected electronic states and robust surface conduction, represent a frontier in quantum materials research. Their non-trivial band topology enables dissipationless edge states, spin-momentum locking, and resilience to disorder, making them strong candidates for spin-orbit torque devices, magnetic field sensors, and polarized light detectors, to name a few. These properties have positioned topological materials as important material of interest as development of scalable quantum technologies grows.

In this study, we explore the atomic and electronic properties of the bismuthine-terminated topological semimetal Bi2-Bi2Se3 using scanning tunneling microscopy (STM) and conductive atomic force microscopy (C-AFM). Bi2-Bi2Se3 is an intrinsic superlattice material s comprised of a Bi2Se3 quintuple layer (QL) slab and a 2D Bismuthine (Bi2) layer separated by a van der Waals gaps. The topological surface state on the 001 orientation depends on the terminating layer, with two distinct possible topologically protected surface states.

The unique step heights between the Bi2Se3 QL and Bismuthine layer enable termination characterization through careful step height analysis. Atomically resolved STM measurements on a Bismuthine terminated step reveal a distinct honeycomb lattice, while scanning tunneling spectroscopy (STS) captures a Dirac cone in local density of states centered at the Fermi level, in excellent agreement with angle-resolved photoemission spectroscopy (ARPES).

Using C-AFM under ambient conditions, we investigate force-dependent I–V spectroscopy. Utilizing step height analysis, we find a bismuthine terminated step and perform point spectroscopy. At low applied forces, differential conductance (dI/dV) spectra reveal a Dirac cone, mirroring STM results and confirming the presence of topologically protected surface states even under ambient conditions! As mechanical force increases, we observe a transition in transport behavior, from quantum tunneling to Ohmic conduction. Additionally, a voltage and force-dependent crossover from direct tunneling to Fowler–Nordheim tunneling is identified.

Our findings revealing the atomic structure and Dirac cone of the bismuthine termination in the topological semimetal Bi2-Bi2Se3. Interestingly these feature are observable even under ambient condition. We find no degradation with time, freshly grown sample versus those that have sat for months give the same results.

3:30pm **2D+AQS+MI+NS+QS+TF-ThA-6 Local Spectroscopy Study of Gate-controlled Energy Gap in Monolayer 1T'-$WTe_2$*, Tiancong Zhu,*** Purdue University*; Zehao He,* University of California at Berkeley*; Michal Papaj,* University of Houston*; Samuel Stolz,* Department of Physics, University of California, Berkeley*; Tianye Wang, Canxun Zhang, Yan-Qi Wang, Joel Moore, Zi Qiang Qiu, Feng Wang, Michael Crommie,* University of California at Berkeley

The interplay between strong correlation and topology can lead to intriguing quantum phases of matter. In monolayer 1T'-$WTe_2$, the non-trivial topology gives rise to the quantum spin Hall insulator (QSHI) phase, characterized by helical 1D edge states surrounding the insulating 2D bulk. While experimental evidences support quantized conductance through the 1D helical edge states, the nature of the insulating bulk, whether attributed to spin-orbit coupling or strong correlation, remains under debate. Here, we employ scanning tunneling microscopy and spectroscopy (STM/S) on gate-tunable 1T'-$WTe_2$ devices to shed light on this problem. Our samples are fabricated using a combination of molecular beam epitaxy (MBE) and van der Waals (vdW) stacking technique, which allows us to synthesize high-quality monolayer 1T'-$WTe_2$ films on a gate tunable graphene field effective transistor supported by hBN. Gate-dependent STS reveals a substantial energy gap in 1T'-$WTe_2$ at its charge neutrality, which diminishes when the Fermi level is tuned into either the conduction or valence band. STS across the sample edges shows that the edge states persist at all gate voltages, while Fourier transform-STM measurement in the bulk further shows the evolution of the bulk band structure at different carrier densities. We will compare our experimental data with existing theoretical models, such as the SOC-induced gap and the proposed excitonic insulator phase, and suggest future experimental directions to further elucidate the origin of the energy gap.

3:45pm **2D+AQS+MI+NS+QS+TF-ThA-7 Exploring Moiré Magnetism in Twisted Two-Dimensional Magnets*, Liuyan Zhao,*** University of Michigan **INVITED**

Moiré superlattice emerges from the interference between two mismatched atomic lattices, and it has led to tremendous success in designing and tailoring the electronic states in two-dimensional (2D) homo- and hetero-structures. Yet, the power of moiré superlattice in controlling the spin degree of freedom and thus modifying the magnetic states is much less explored. Only very recently after the development of 2D magnet research, there have been a few experimental attempts in realizing moiré magnetism in twisted 2D magnet homo-structures. In this talk, I will show our recent effort in studying magnetic phases in twisted double bilayer chromium triiodide (CrI3) and progressive steps towards realizing moiré magnetism. Noting that bilayer CrI3 is a layered antiferromagnet and that any homogeneous stacking of two bilayers necessarily produces zero magnetization, we have revealed, in twisted double bilayer CrI3, an unexpected net magnetization showing up at intermediate twist angles and its accompanied noncollinear spin textures. I will show the optical spectroscopy signatures of this twist-induced magnetic phase, then discuss its dependence on twist angle, external magnetic field, and temperature.

## Atomic Scale Processing Mini-Symposium
## Room 206 A W - Session AP+PS+TF-ThA

### Emerging Applications for Atomic Scale Processing (ALD/ALE) including Precursors and Surface Reactions
**Moderator: Robert Bruce**, IBM Research, T. J. Watson Research Center

2:15pm **AP+PS+TF-ThA-1 ALD Thin Films for Protecting Limestone Cultural Heritage*, Gillian Boyce,*** *Suveena Sreenilayam,* University of Maryland, College Park*; Eleonora Balliana, Elisabetta Zendri,* Università Ca' Foscari Venezia, Italy*; Raymond Phaneuf,* University of Maryland, College Park

From natural erosion to pollution-accelerated decay, stone cultural heritage deteriorates constantly through interactions with the environment. Common protective treatments such as acrylic polymers are generally prone to degradation and loss of performance, and they are often limited in their ability to achieve uniform and conformal coverage across a stone's topographical features. In this work, we report on the results of investigations of atomic layer deposited (ALD) amorphous alumina thin films for the protection of calcium carbonate substrates of a wide range of porosity against acid-based dissolution. The protective effects of the ALD coatings were investigated by aqueous acid immersion. The solution pH was tracked over time for a constant volume of acetic acid solution with an initial pH of 4 with the stone samples immersed. We find the protective effect of ALD alumina coatings is extremely promising, with 90 nm thick coatings slowing the average rate of pH evolution significantly, by between one and two orders of magnitude, depending on the porosity of the substrate. The eventual failure of the ALD coatings during immersion was also investigated, with the development of pits on the substrates, whose area fraction correlates to the changing pH of the acid solution during immersion. The variation of the protective action of the films with thickness is consistent with kinetics which are limited by diffusion within the pits, rather than through the films. Our findings point to the dominant role of defects in the thin films in their eventual failure

2:30pm **AP+PS+TF-ThA-2 Atomic Layer Depositionon Ceramic NanopowdersforPrecisely Engineered Microstructure of Sintered Ceramics***, **Eric Bissell**, Alexandros Kostogiannes, Steve Lass, Anna Zachariou, Brian Butkus, Luis Tomar, Terrick Mcnealy-James, Ayelen Mora, Blaine Mauri-Newell,* University of Central Florida*; Nicholas Rudawski,* University of Florida, Gainesville*; Romain Gaume, Parag Banerjee,* University of Central Florida

In this work, we have utilized the conformal nature and monolayer control of growth of ALD films to develop ≤ 10 nm, ultrathin diffusion barriers on the surfaces of ceramic nanoparticles. The barrier layer restricts grain growth during sintering leading to formation of bulk, nanocrystalline ceramics which demonstrate unique properties such as superior hardness and optical transparency, otherwise not achievable using traditional powder preparation and sintering steps.

Zinc oxide (ZnO) nanoparticles of 60 nm nominal diameter were coated with 1 or 10 nm of Al2O3in a custom-built, rotary ALD powder reactor. In situ mass spectrometry was used to end point the half-reaction pulse times. The powder was subsequently mixed at a 1:1 mass ratio with uncoated ZnO nanoparticles where the uncoated ZnO served as the 'control' sample undergoing the exact thermal and pressure cycling as the coated regions. The powder mixtures were subsequently compacted and hot pressed at 850 °C under uniaxial loading of 150 MPa. The sintered ceramics reveal that the 1nm and 10nm 'shell' Al2O3 layers effectively restrict grain size of the ZnO to 89 ± 23 nm and 55 ± 7 nm respectively, whereas the uncoated regions grow large polycrystalline grains of 601 ± 104 nm and 717 ± 80 nm respectively. The crystal structure analysis reveals ZnO in its thermodynamically stable wurtzite phase with no evidence of secondary phase formation. This study demonstrates the broad applicability of ALD based coating technology to the field of ceramics for fine microstructural control and precise tunability of bulk properties.

2:45pm **AP+PS+TF-ThA-3 Hot-Wire-Assisted Atomic Layer Deposition of Transition Metals***, **Kyeongmin Min**, Han-Bo-Ram Lee,* Incheon National University, Republic of Korea

To replace conventional Cu interconnects, atomic layer deposition (ALD) of low figure-of-merit (FOM) materials such as cobalt (Co) and nickel (Ni) is crucial. While noble metals have been extensively studied as alternative interconnect materials due to their excellent performance, the high cost necessitates the development of low cost materials with superior properties. However, existing Co and Ni ALD processes inevitably require plasma to achieve high purity, leading to inherent limitations such as poor step coverage due to radical recombination and unavoidable damage to 3D structures caused by energetic ions and photons. In this study, we studied transition metal ALD processes using a hot-wire-activated counter reactant, enabling the deposition of high-purity films without generating energetic ions or photons. $NH_x$ radicals were generated by exposing $NH_3$ counter reactant gas to a filament heated over 1300 °C. Due to the high thermal energy of the filament, $NH_3$ gas molecules dissociated into high energy radicals, which played a crucial role as reactants in the transition metal ALD processes. The concentration of $NH_x$ radicals was studied as a function of the hot wire temperatures and correlated with the physical properties of films. The purity of transition metal films was analyzed using X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES). Based on the results of this study, we believe that the hot-wire-assisted ALD process can be widely utilized in various applications where overcoming the limitations of conventional plasma ALD is essential.

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3:00pm **AP+PS+TF-ThA-4 Ni Thin Film Deposition Using Hot Wire ALD and Non-Halogen Precursor***, **Mruthunjaya Uddi**, Mike Denchy, Prawal Agarwal, Josh Kintzer, Patryk Radyjowski,* Advanced Cooling Technologies Inc.

Scale up of pure phase nickel (Ni) thin film deposition process for various applications of catalysis, microelectronics, chemical sensors, and MEMS, especially, using environmentally friendly non-halogen precursors is challenging. ALD is a variation of Chemical Vapor Deposition (CVD), with the complete metal deposition reaction broken into two half steps. Since each half-step saturates at a single atomic layer, a very precise control over deposition can be achieved. Although slower than CVD deposition rates, ALD can enable precise, uniform, conformal coating of Ni thin films. Recently, we assembled an automated Hot Wire Atomic Layer Deposition (HW-ALD) reactor and demonstrated Ni thin film deposition using a non-halogen precursor nickelocene and $NH_3$. The hot wire implementation enabled the non-halogen chemistry pathway. The details of reactor design, operation parameters and characterization of the Ni thin film deposited will be presented. Future experiments will involve large area (> 15 cm diameter) substrate coating with Ni thin films and the uniformity of distribution will be studied.

3:15pm **AP+PS+TF-ThA-5 Pyroelectric Calorimetry for ALD***, **Ashley Bielinski**,* Argonne National Laboratory

A deeper understanding of the self-limiting surface reactions that make up and ALD processes is vital for the development of many emerging applications such as area and site selective ALD processes that rely on chemical differentiation between a range of surface sites. Natural variation and defects in real surfaces necessitate in situ measurements of these surface reactions in order to develop a complete picture of the process. These in situ measurements can be combined with computational results on simplified model surfaces to help understand not only the single most favorable reaction pathways but also changes in the reactions as surfaces dynamically approach saturation and reactions on a realistic range of surface conditions.

Pyroelectric calorimetry can be used to quantitatively measure the heat evolved during an ALD surface reaction with high time resolution within a single saturating precursor reaction. This approach has been used to measure the reaction enthalpy of various ALD precursor reactions during the deposition of $Al_2O_3$, $ZrO_2$, and MgO. Analysis of the heat generation rate profiles of these processes in combination with techniques such as in situ spectroscopic ellipsometry and quartz crystal microgravimetry have provided insight into properties including multi-step reaction mechanisms and the driving role of entropy in certain reaction mechanisms. Recent hardware developments further enable measurements of precursor delivery and reaction kinetics. Knowledge of the mechanisms, thermodynamics, and kinetics of these reactions will guide the development of future ALD processes and provide the necessary parameters for the development of more complex and accurate computational models.

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3:30pm **AP+PS+TF-ThA-6 Fabrication of Atomically-Precise Nanoimprint Masks by STM Lithography***, **James Owen**[1], Ehud Fuchs, John Randall,* Zyvex Labs

The Semiconductor industry is struggling to continue to follow Moore's Law. For both technical and economic reasons, it is likely that the ASML High-NA Extreme Ultraviolet Lithography (EUV) tools will be the last photolithography technology to push to higher resolutions. Simultaneously, E-Beam Lithography (EBL) mask writers, while improving throughput by going highly parallel, are also very near the end of resolution improvements. The industry does not appear to expect any significant

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[1] **JVST Highlighted Talk**

downscaling of devices beyond what will be possible with the ASML High-NA EUV tool which has a resolution of 8 nm.

The DOE Advanced Materials and Manufacturing Technologies Office (AMMTO) sponsored Semiconductor Industry Energy Efficiency Scaling (EES2) roadmap has identified EUV as a significant contributor to the energy budget of advanced digital electronics. Strikingly, EUV is so inefficient that only about 0.04% of the beam energy actually affects the resist. The EES2 roadmap proposes that replacing EUV with Nanoimprint lithography (NIL) would be a way to improve the energy efficiency of semiconductor manufacturing. NIL offers equal and better resolution and precision than EUV, with up to 90% lower energy costs, resulting in lower costs of production. However, NIL uses a mold of the pattern to be printed on the wafer as a mask and the best resolution of the current EBL mask writers is 15nm. Therefore, a mask writing technology with better resolution than EBL is required; it must provide resolution at least as good as the High NA EUV tool's 8nm to be widely adopted.

We describe a pathway towards unprecedented resolution in nanoimprint mask fabrication. Ultrahigh-precision NIL templates are made by writing sub-nm-precision patterns on Si(001) using Scanning Tunnelling Microscope(STM) lithography followed by selective growth via atomic layer deposition of a hard mask such as $TiO_2$, which is then used as an etch mask for Reactive Ion Etching to form a Si template, replicating the STM pattern. This template would then be transferred into a quartz template using existing step and flash NIL processes which will then be used to pattern devices on the die or wafer scale. We show that sub-10 nm feature sizes and full-pitch gratings with feature radius of curvature down to 1.5 nm in the lateral dimension are achievable, although the throughput is currently much too slow to be industrially feasible at the moment. This process therefore addresses the EES2 goal of improving the energy efficiency during manufacturing of digital electronics.

3:45pm **AP+PS+TF-ThA-7 Three-In-One Isolation New Integration Solution for Monolithic CFET***, Junjie Li, Longrui Xia,* Institute of Microelectronics of the Chinese Academy of Sciences, China*; **Mingmei Wang,*** Lam Research Corporation

***Introduction:*** Monolithic complementary transistors (CFET) will replace gate all around field-effect transistor (GAA FET) in technology nodes below 1nm [1].CFET stacks N-type transistors on top of P-type transistors to reduce footprint and increase transistor density. Therefore, it is important to isolate the gate and source drain, as well as the gate of the upper and lower transistors. The current publicly available solution is to isolate the gate and source drain of the outer wall and inner wall, and isolate the gate of the upper and lower transistors with an intermediate isolation layer (MDI). This is achieved through three process steps, requiring at least three atomic layer deposition and atomic layer etching[2] (figure 1 of supplemental material). In order to simplify the process and reduce its difficulty, this article proposes a new process integration scheme that combines the above three steps into one deposition step and one etching step to achieve.

***Results and Discussion*** :

***Conclusion:***We conducted a detailed comparison between the publicly available CFET process flow and the new process flow proposed in this article, as shown in Figure 2 f supplemental material, and ultimately successfully implemented a new three-in-one integrated solution of inner and outer side spacers and MDI. And demonstrated the results of key intermediate steps such as concave dummy gate and $CH_x$ dummy gate self-aligned etching source drain.

***Reference:***

【1】 C. Cavalcante, VLSI, (2025).

【2】 T.Lill, VLSI (2025).

4:00pm **AP+PS+TF-ThA-8 New Silicon-containing Precursors for Metal Silicide Films***, **Sean Barry,** Dexter Dimova,* Carleton University, Canada

Group 3 metals, particularly scandium and yttrium, offer tunable electropositivity when incorporated in thin films. They are attractive for next-generation microelectronic applications, including silicide and germanide thin films in gate-all-around FET architectures. However, suitable precursors for vapor phase deposition of lanthanide films remain scarce. In this work, we explore a new family of geminal diamidosilane (gDAS) ligands, designed for both homoleptic and heteroleptic coordination to Group 3 centers. These ligands provide modular steric control and enhanced volatility, allowing for the design of thermally stable precursors.

We report the synthesis and characterization of several Sc and Y complexes with methyl- and tert-butyl-substituted gDAS ligands. Thermogravimetric and isothermal analyses reveal decomposition pathways involving γ-hydride elimination, which is critical for understanding volatility and thermal stability in thin film deposition. Notably, $Y(gDAS)_3$ precursors exhibit promising volatility, while extended thermolysis suggests silicide incorporation may be feasible under atomic layer deposition conditions. We also demonstrate preliminary hydrogenation and dehydrocoupling strategies to prepare silicon-containing intermediates compatible with gDAS ligand frameworks. This presentation will show the groundwork for tailored ligand design strategies that enable selective, low-temperature deposition of lanthanide-silicon films.

4:15pm **AP+PS+TF-ThA-9 Conversion-free Atomic Layer Etching of ZnO Using Hydrofluoric Acid and Trimethylgallium for Reduced Residues***, **Taewook Nam,*** Sejong University, Republic of Korea*; Steven George,* University of Colorado Boulder

Thermal atomic layer etching (ALE) is a crucial technique for advanced semiconductor manufacturing, offering precise material removal with sub-nanometer control. While various etching mechanisms exist, including the widely used fluorination-ligand exchange reaction, some materials are etched via a "conversion" mechanism where the original material is converted into a different compound before being removed. This conversion-based ALE, as seen in zinc oxide (ZnO) etching with hydrofluoric acid (HF) and trimethylaluminum (TMA), can leave undesirable residues of the converted material, $Al_2O_3$, on the surface, which is detrimental for fabricating high-performance, sub-nanometer scale devices.

In this study, we present a novel, conversion-free thermal ALE process for ZnO using HF and trimethylgallium (TMG) as precursors. This alternative chemistry was investigated using a suite of characterization techniques, including quartz crystal microbalance (QCM) and quadrupole mass spectrometry (QMS). ZnO films were initially grown via atomic layer deposition (ALD) using diethylzinc (DEZ) and water at 100°C. QCM measurements during the ALE process showed self-limiting mass gain during HF exposure and mass loss during TMG exposure, confirming the characteristic digital nature of the process. The etch rate was found to increase with temperature, reaching 3.82 Å/cycle at 300°C.

A significant advantage of the HF-TMG process is its ability to etch at temperatures as low as 30 °C, which is dramatically lower than the ≥ 240 °C required for the conventional HF-TMA process. This difference in temperature is attributed to the distinct reaction mechanisms of the metal precursors. While TMA exposure converts ZnO to $Al_2O_3$, enabling the subsequent unwanted deposition of $AlF_3$ during HF exposure, TMG exposure results in mass gain from precursor adsorption without conversion. The absence of this competing ALD reaction allows for effective, low-temperature ALE with HF-TMG. QMS analysis further supports this, showing no evidence of conversion and confirming a fluorination-ligand exchange mechanism.

The conversion-free nature of the HF-TMG process also leads to a notable reduction in residual contamination on the etched surface. X-ray photoelectron spectroscopy (XPS) confirms that the HF-TMA process leaves significant concentrations of both F (8.6 at.%) and Al (8.9 at.%) on the surface after ALE. In contrast, the HF-TMG process results in much lower residual concentrations of both F (1.1 at.%) and Ga (2.4 at.%).

## Thin Films
## Room 206 B W - Session TF+CPS+MS+EM-ThA

### Thin Films for Microelectronics II

**Moderators: Lauren Garten**, Georgia Institute of Technology, **Christophe Vallee**, University at Albany

2:15pm **TF+CPS+MS+EM-ThA-1 Area Selective Deposition Processing in the Memory Industry: How to Take Advantage of the High-Volume Manufacturing Environment***, **Francois Fabreguette,** Jeff Hull, Huicheng Chang, Erik Byers, Gurtej Sandhu,* Micron Technology **INVITED**

Aggressive scaling from node to node in the memory industry has led to a paradigm shift towards Area Selective Deposition (ASD) technique to overcome traditional processing challenges. For example, punches or etches not being capable anymore in High Aspect Ratio structures >100:1 can be replaced by selective deposition processes on the sidewall only, eliminating the need to clear a bottom contact. Likewise, ASD can be used to heal a contact seam that can easily form when the deposited metal pinches off at the top of a High-Aspect ratio structure, leavinga void in the middle of the filled contact. Finally, in tiered structures used for 3D memory scaling, ASD allows for dielectric re-deposition on one tier type selective to the other tier type for cell sculpting without any critical dimension penalty.The present abstract covers a few examples of ASD processes developed in Micron High Volume Manufacturing environment:The state-of-the-art 300mm wafer tooling capability as well as multiple full-wafer inline metrology techniques (such as X-Ray fluorescence, X-ray Photoelectron Spectroscopy, X-Ray Reflectivity, Ellipsometry, Atomic Force Microscopy) allows to characterize the loss of selectivity on the non-growth surfaces on wafer-level. This provides across-wafer inhibition efficiency, which is criticalfor Area Selective Deposition future adoption in large scale production. The case study of ASD TiN using new high-temperature oxide inhibitors is presented. The systematic inline metrology characterization of the inhibited blanket oxide surfaces after TiN deposition at various temperatures is used to determine the best selectivity conditions as well as individual inhibitor performance benchmarked to the best-known oxide inhibitor typically used in the ASD community. Besides, Fourier Transform Infrared (FTIR) spectroscopy, Water Contact Angle measurements (WCA) and carbon content from XPS measurements were performed immediately after inhibition. Theyprovided the surface signature of each inhibitor and were correlated to their overall inhibition efficiency.

2:45pm **TF+CPS+MS+EM-ThA-3 BEOL-compatible (≤300 °C) top-gate $HfO_2$/ZnSnO Transistors Enabled by Atomic Layer Deposition for Advanced Memory Integration***, **Changyu Park**, Jinsung Park, Joohee Oh, Hyoungsub Kim,* Sungkyunkwan University, Republic of Korea

Amorphous oxide semiconductors (AOSs) are promising channel materials for three-dimensional (3D) dynamic random-access memories (DRAMs) owing to their structural uniformity from a stable amorphous phase, low-temperature processability, and extremely low off-state current enabled by their wide bandgap [1]. Atomic layer deposition (ALD) further enhances their applicability by offering conformal coverage in high-aspect-ratio structures and high film quality at low processing temperatures. Among the various AOSs, zinc tin oxide (ZTO) is particularly attractive due to its efficient carrier transport, facile composition tunability, reliance on earth-abundant elements, and high thermal stability [2]. For back-end-of-line (BEOL) integration in 3D DRAM, ZTO must be combined with ALD-grown high-κ dielectrics in top-gate architectures; however, most previous studies have primarily focused on bottom-gate thin-film transistors (TFTs) [3,4].

In this work, we demonstrate the fabrication and characterization of top-gate TFTs with ZTO channels and $HfO_2$ gate dielectrics, both integrated via ALD at temperatures up to300 °C for BEOL-compatible processing. Guided by the ALD growth behavior of ZnO and $SnO_2$, ZTO films with various compositions were deposited using a super-cycle method with diethylzinc (DEZ) and tetrakis(dimethylamino)tin(Ⅳ) (TDMASn) at 250 °C, employing ozone ($O_3$) as the oxidant. After annealing of the ZTO channel at 300 °C for 1 h in ambient air, indium tin oxide source/drain electrodes were formed. The $HfO_2$ gate dielectric was subsequently deposited via ALD using $O_3$ at 230 °C.The extracted average parameters of top-gate TFTs with an optimized ZTO composition confirmed their suitability for DRAM cell operation, exhibiting a threshold voltage ($V_{th}$) of 0.15V, a saturation mobility of 4.3$cm^2$/V·s, a subthreshold swing of 76mV/dec, and an on/off current ratio exceeding $10^7$. Device reliability was further evaluated through positive and negative bias stress tests at ±3 MV/cm, resulting in $V_{th}$ shifts of +0.47 V and –0.12 V, respectively, which are comparable to recent reports on bottom-gate device configuration [3].

[1] A.R. Choi *et al.*, Chem. Mater. **36**, 2194 (2024)

[2] B. Lu *et al.*, Curr. Opin. Solid State Mater. Sci. **27**, 101092 (2023)

[3] J. Choi. *et al.*, ACS Appl. Electron. Mater. **7**, 215 (2025)

[4] J.S. Hur *et al.*, Nanoscale Horiz. **9**, 934 (2024)

3:00pm **TF+CPS+MS+EM-ThA-4 Photoluminescence Spectroscopy of Ultra-Thin GeSn Alloys Grown on Ge-on-Si Substrates***, **Vijay Gregory**, Lia Guo, Jay Mathews,* University of North Carolina at Charlotte

Silicon (Si) based devices have dominated the electronics industry over the past decades but are not suitable for making lasers due to their optical properties. As an indirect bandgap semiconductor, Si has inefficient optical emission and therefore cannot be used to make a light source on a Si chip. As an alternative, germanium (Ge), incorporated with tin (Sn), can be grown on Si and is currently being used for photonic devices. GeSn exhibits direct bandgap emission at room temperature and is ideal for an on Si light source. However, they suffer from low intensity due to high defect densities which cause nonradiative recombination.

In this work, we study GeSn/Ge/Si samples with varying percentages of Sn. The materials were grown with sub 100 nm thickness resulting in fully strained thin films which reduce the dislocations caused by lattice relaxation. The emission spectrums of these ultra-thin layers were measured using photoluminescence (PL) spectroscopy to probe the quality of the materials as on Si light sources.

3:15pm **TF+CPS+MS+EM-ThA-5 Highly Ordered NiO (111) Films on Sapphire Substrates via Low-Temperature Hollow Cathode Plasma-ALD and Their Post-Deposition Annealing Characteristics***, Fatih Bayansal, Steven Allaby, Habeeb Mousa, Helena Silva, **Necmi Biyikli**,* University of Connecticut

Nickel oxide (NiO) is a promising p-type wide band gap semiconductor material for next generation optoelectronic and energy devices. In this study, the growth process and thermal annealing behavior of NiO thin films grown on c-plane sapphire substrates by hollow-cathode plasma-assisted atomic layer deposition (HCP-ALD) method were investigated. $NiCp_2$ was used as the nickel precursor heated at 100°C, and $O_2$ plasma was preferred as the oxidizing agent under 100W rf-power and 20 sccm flow rate. The films were grown within a substrate temperature range of 100 – 250°C.

The obtained film samples showed high transmittance in the visible spectrum and exhibited strong absorption in the UV spectrum. Optical band gap values determined by Tauc analysis were found between 3.54 and 3.59eV. The refractive indices increased with the growth temperature and reached 2.38, while the extinction coefficient and film porosity decreased for higher temperature films. X-ray diffraction (XRD) analyses revealed that the films exhibit a highly textured structure with exclusive (111) orientation. No peaks belonging to any other phase or crystal plane were observed. Moreover, grazing incidence XRD (GIXRD) measurements showed no detectable peaks, confirming the monocrystalline film character, and suggesting a surface-parallel alignment and potentially dense and thin film morphology. In addition, shifts in the diffraction peaks were observed depending on the growth temperature.

In order to evaluate the thermal stability and performance of the films, the samples grown at 250°C were annealed at 300, 350 and 400°C. Ongoing studies include characterization of electrical properties (Hall effect) such as carrier density, mobility and conduction type as well as crystal structure (XRD, TEM) and chemical composition (XPS). This holistic approach will contribute to understanding the impact of post-deposition annealing on the crystal quality and charge transport properties of NiO films.

This work contributes to the development of optimized p-type oxide semiconductors for transparent electronics and heterojunction-based devices through controlled low-temperature ALD process and post-deposition thermal engineering.

3:30pm **TF+CPS+MS+EM-ThA-6 Textured Growth and Electrical Characterization of Zinc Sulfide on Back-End-of-the-Line (BEOL) Compatible Substrates***, **Claire Wu**, Mythili Surendran, Anika Priyoti, Gokul Anilkumar,* University of Southern California*; Chun-Chen Wang,* Taiwan semiconductor Manufacturing Company, Taiwan*; Cheng-Chen Kuo, Cheng-Hsien Wu,* Taiwan Semiconductor Manufacturing Company, Taiwan*; Rehan Kapadia,* University of Southern California*; Xinyu Bao,* Taiwan Semiconductor Manufacturing Company, Taiwan*; Jayakanth Ravichandran,* University of Southern California

Scaling of transistors has enabled continuous improvement in the performance of logic devices, especially with recent advances in materials engineering for transistors. However, there is a need to surpass the horizontal limitations in chip manufacturing and incorporate the vertical or third dimension. To enable monolithic three-dimensional (M3D) integration of high-performance logic, one needs to solve the fundamental challenge of low temperature (<450 °C) synthesis of high mobility n-type and p-type semiconductor thin films that can be utilized for fabrication of back-end-of-line (BEOL) compatible transistors.1 Transition metal oxides are promising n-type materials; however there is a lack of p-type materials that can meet the stringent synthesis conditions of BEOL manufacturing. Zinc sulfide (ZnS), a transparent wide band-gap semiconductor, has shown room temperature p-type conductivity when doped with copper2 and crystallizes below 400oC when grown by pulsed laser deposition (PLD).3 Here, we report growth of crystalline thin films of ZnS by PLD on a variety of amorphous and polycrystalline surfaces such as silicon nitride, (SixNy) thermal silicon dioxide, (SiO2), hafnium dioxide, (HfO2), yttrium oxide (Y2O3), platinum, sapphire (Al2O3), and titanium nitride (TiN). X-ray diffraction shows texturing of ZnS on all surfaces, including when ZnS is directly grown on HF buffered oxide etched silicon. Crystalline quality is investigated using grazing incidence wide angle X-ray scattering measurements. Surface and interface quality is measured using X-ray reflectivity and atomic force microscopy measurements. Electrical characterization of the ZnS films is done by J-V measurements of ZnS on platinum and metal-oxide-semiconductor capacitor (MOSCAP) measurements of ZnS on SiO2 on heavily doped silicon. The J-V measurements indicate low leakage current on the order of 10-8 A/cm-2 with electric field of 0.013 MV/cm2 and the MOSCAP characteristics show bilayer capacitor behavior, which points to ZnS being highly intrinsic with very low unintentional, electrically active point defects. Further work on doping ZnS with copper or other p-type candidate dopants are needed to demonstrate ZnS as a dopable wide band gap semiconductor for channels compatible with BEOL manufacturing. This work showcases the capability of novel thin film growth technique of a wide band-gap sulfide semiconductor in BEOL compatible conditions with potential for technological applications in transistor manufacturing.

1. S. Datta et al., IEEE Micro.39, 6, 8-15 (2019)

2.R. Woods-Robinson et al., Adv. Electron. Mater. 2, 1500396 (2016)

3. M. Surendran et al., Adv. Mater. 36, 2312620 (2024)

3:45pm **TF+CPS+MS+EM-ThA-7 Thermal Atomic Layer Deposition of Molybdenum Phosphide Films***, John D. Hues, Wesley Jen,* ***Nolan Olaso,*** *Steven M. Hues, Elton Graugnard,* Boise State University

Aggressive scaling of semiconductor technology nodes has led to copper-based interconnects beginning to approach the maximum scaling limit of the material, beyond which unacceptably high increases in interconnect resistance due to electron scattering at grain boundaries and interfaces begins to cause degradation of device performance. New materials are required for interconnect applications beyond the 7 nm node to produce devices with acceptable signal delay and power consumption parameters. Topological semimetals are one family of materials that are of interest for the replacement of copper in interconnect applications due to the predicted favorable resistance scaling, which results from topologically protected surface states that suppress electron scattering and act as conduction pathways in nanoscale films. This decrease in interconnect resistance has the potential to improve the efficiency of integrated circuits through reduced RC delay and reduced energy consumption, which is under increased scrutiny due to increasing computing demands, such as generative artificial intelligence and cloud computing. In order to aid in the integration of these promising materials into production environments, scalable synthesis methods, such as atomic layer deposition (ALD), are needed. In addition to the development of deposition chemistries for these materials, insight into how processing conditions impact the performance of the resulting film are also of importance. Here, we report on a new thermal ALD deposition chemistry for molybdenum phosphide (MoP) using molybdenum(V) chloride ($MoCl_5$) and tris(dimethylamino)phosphine (TDMAP) at temperatures between 350 °C and 425 °C. In-situ and ex-situ characterization of the resulting films was performed using quartz crystal microbalance (QCM), x-ray photoelectron spectroscopy (XPS), x-ray diffraction (XRD), atomic force microscopy (AFM), scanning electron microscopy (SEM), and four-point probe measurements. QCM measurements demonstrated a linear mass increase of 164 ng/cycle at 375 °C. Film deposition was confirmed through XRD and XPS chemical state analysis. The resulting films were near stoichiometric as determined via XPS. AFM and SEM characterization revealed a polycrystalline morphology with nanoscale grain sizes. Four-point probe measurements of the as-deposited films indicated non-ideal electrical performance which was subsequently improved through post deposition annealing. Although more work is needed to improve electrical performance, this new ALD chemistry may provide a method for the deposition of MoP films at the dimensions required for next generation technology nodes.

## Thin Films
## Room Ballroom BC - Session TF-ThP
## Thin Film Poster Session

**TF-ThP-1 Thickness and Elemental Quantification of (Ultra)Thin Films Revisited***, **Markus Sauer**, Jakob Rath, Annette Foelske,* TU Wien / AIC, Austria*; Dieter Ingerle,* TU Wien / XRC, Austria

Many approaches have been taken towards precise determination of overlayer thickness and (elemental) quantification of thin/ultrathin films (0.5-100nm). X-ray reflectivity (XRR) and X-ray photoelectron spectroscopy (XPS) as well as spectroscopic ellipsometry are commonly used to provide information about sample composition and layer depth (1-3). However, each of these methods has its limitations and specific techniques/sample geometries etc. might require extensive preparation and or do not allow for the use of ultra-high vacuum instrumentation. In addition, some of these methods as well as alternatives like Rutherford Backscattering/Elastic Recoil Detection Analysis (RBS/ERDS) require expensive equipment and/or access to large-scale facilities which is not always an alternative in every day-use cases.

Herein we report a broad comparison of different techniques including most of the above-mentioned ones (XPS, SEM-EDX, XRR, Ellipsometry) as well as Auger-Meitner Electron Spectroscopy (AMES), X-ray fluorescence (WXRF and GIXRF) and Raman spectroscopy for two sets of reference materials: $HfO_2$ on $SiO_2$/Si (4) and Fe/Ni thin films with different relative compositions.

We provide an approach for choosing different methods and method combinations depending on the requirements/sample surface size/roughness etc. for laboratory scale application beyond the reference material case. In addition, limitations of each method in terms of precision and applicability are discussed.

A roadmap is laid out for finding the most useful way of reaching the desired precision for quantification and thickness determination trying to use methods that are available to a large number of researchers in academia and industry.

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**TF-ThP-3 Electrical and Mechanical Stability of Flexible Low-Dielectric Constant Carbon-Doped Oxide (SiCOH) Thin Films Under Repeated Mechanical Stress***, **Rajib Chowdhury**[1], SeonHee Jang,* University of Louisiana at Lafayette

The microelectronics industry continuously advances materials science to enhance integrated circuit (IC) performance. Interconnect structures are becoming critical as the transistor density increases. It also limits the chip speed due to increased resistance-capacitance (RC) delay. Traditionally, aluminum (Al) and silicon oxide ($SiO_2$) were utilized as metal and dielectric materials, which were replaced with copper (Cu) and low dielectric constant carbon-doped silicon oxide (low-*k* SiCOH, $k < 4$) to improve the RC delay and power consumption. Simultaneously, flexible electronics have gained attention, utilizing polymer substrates for applications like wearable devices and displays. However, integrating low-*k* flexible dielectric films with polymer-based substrates remains challenging due to the low glass transition temperatures of the substrates. Besides, it is essential to study the mechanical stability of materials for the integration of flexible electronic devices. This study explores the applicability of the low-*k* SiCOH thin films for flexible electronics by observing the effects of repeated mechanical bending tests.

Flexible low-*k* SiCOH films were produced onto flexible indium tin oxide-coated polyethylene naphthalate (ITO/PEN) substrates by plasma-enhanced chemical vapor deposition (PECVD) of a tetrakis (trimethylsilyloxy)silane precursor. The films were deposited at room temperature with the RF plasma power varied from 20 to 100 W. The films were subjected to bending tests with up to 10000 bending cycles. Mechanical characterization was performed by nanoindentation testing for the elastic modulus and hardness. Chemical bonds were characterized by Fourier transform infrared (FTIR) spectroscopy, and the atomic concentration was measured by X-ray photoelectron spectroscopy (XPS). The dielectric constant was measured from capacitance-voltage measurements.

The pristine SiCOH films had a mechanical strength of up to 9.1 GPa and a low *k*-value down to 2.00. The films were optically transparent, smooth, and hydrophobic. The prominent chemical peaks of $CH_x$, Si-$CH_3$, Si-O-Si, and Si-$(CH_3)_x$ were identified for pristine films from the analysis of FTIR spectra. Upon repeated mechanical bending tests with bending cycles up to 10,000, the flexible SiCOH films maintained their transparency, smoothness, and hydrophobicity and showed a stable *k*-value below 4.0. No significant changes in the FTIR spectra were observed, and no cracks or delamination were observed in the films. The SiCOH films showed stable physical, chemical, and electrical properties under repeated mechanical bending.

**TF-ThP-4 The Impact of Copolymer Molecular Sequence on Electronic Transport***, **Mahya Mehregan**, Jack Schultz,* University of Missouri-Columbia*; Matthew Maschman, Matthias Young,* University of Missouri, Columbia

This work demonstrates the successful formation of EDOT-co-Py copolymer thin films using oxidative molecular layer deposition (oMLD), with electrical conductivity values intermediate between those of PEDOT and PPy. By controlling the molecular sequence during copolymerization via the sequential surface reactions afforded by oMLD, we investigate the influence of monomer arrangement on electronic conductivity. Our findings reveal that the electrical conductivity of the copolymer thin films is not determined by the composition ratio of EDOT and Py but is instead strongly influenced by the block length of each monomer chain. These block lengths modulate the electron energy well depths for electron transport along the copolymer chains, which in turn affects conductivity. Our analysis reveals that the energy well depth in Boltzmann transport modeling exhibits a sigmoidal relationship with the separation distance between conductive domains, rather than the previously assumed linear dependence. We identified a critical domain size of >3 monomer units (corresponding to 1.4 nm) that significantly alters electronic conductivity, consistent with electron hopping distances observed in biomolecules. This suggests a universal length scale for electronic interactions in polymers.

**TF-ThP-5 Synthesis of Bismuth-based EUV Photoresists using Molecular Layer Deposition***, **Jane Keth**[2], Duncan Reece, David Bergsman,* University of Washington

Extreme ultraviolet (EUV) photolithography has seen substantial interest from the semiconductor industry as a tool to create sub-10 nm features, which are necessary to improve device performance. To use this process, EUV-compatible photoresists are needed that are highly absorbing of EUV light, can be deposited as a thin film, and have high etch resistance. Many photoresist materials have been explored to meet this need, including polymer films exposed to vapor-phase infiltrants, polymer films combined with metal additives, and hafnia-based nanoparticle thin films. However, these resists tend to be limited to low viscosity resist formulations or use deposition methods like spin coating that struggle to form conformal coatings. One promising strategy for creating these resists involves using molecular layer deposition (MLD) to synthesize hybrid inorganic-organic films directly on the surface of interest. MLD is a vapor-phase layer-by-layer thin film deposition process that can deposit films with subnanometer thickness and compositional control. While MLD has been used to make aluminum, hafnium, and tin-based EUV photoresists, films based on other elements may be beneficial. In this work, we will present on using a Bismuth-based MLD process to grow hybrid organic-inorganic EUV photoresists. Using a specialized parallelizing reactor unique to the Bergsman research group, we explore the growth of Bi-based photoresists with different organic linkers, characterizing their composition and testing their ambient stability and chemical stability. After studying the as-deposited resists, we treat the resists to UV light and measure their

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

[2] **JVST Highlighted Poster**

subsequent chemical structure and stability. This data is used to derive the understanding of how Bi-based EUV photoresists can be further optimized for EUV photolithography.

**TF-ThP-6 Hollow-Cathode Plasma-Assisted ALD of CuO Thin Films: Evaluating Self-Limiting Growth Conditions and Material Properties***, Fatih Bayansal, Steven Allaby, Habeeb Mousa, Helena Silva,* ***Necmi Biyikli,*** University of Connecticut

Copper oxide (CuO) is a promising p-type semiconductor material with potential applications for energy and optoelectronic devices. In this study, we conducted a comprehensive saturation study within the scope of our initial attempts to grow CuO films by hollow-cathode plasma-assisted atomic layer deposition (HCP-ALD) followed by material characterization study to evaluate the structural, optical, and electrical properties of grown samples.

During CuO growth experiments, copper(II) hexafluoroacetylacetonate hydrate [$Cu(hfac)_2 \cdot xH_2O$] and $O_2$ plasma were used as the metal precursor and oxidizing agent, respectively. Saturation experiments performed on Si(100) substrates at 150 °C showed that the growth rate reached the saturation regime when the precursor pulse duration increased above a certain threshold. This demonstrated that surface-controlled self-limiting ALD behavior is achieved under appropriate plasma conditions. On the other hand, CuO formation was suppressed in the growths performed using only Ar plasma or $O_2$/Ar mixture, and metallic or non-stoichiometric structures were observed in some samples. These results confirmed the critical role of reactive oxygen species for CuO growth.

After determining the self-limiting growth window, the synthesis temperature was gradually increased to 250°C and film deposition studies were carried out on n-Si, sapphire, and quartz substrates. Initial transmittance measurements showed that as the temperature increased, the films exhibited higher transmittance in the visible region, thus increasing the film smoothness and quality.

X-ray diffraction (XRD) analyses revealed that the films grown in optimized $O_2$ plasma conditions contained polycrystalline CuO phases with (110), (002) and (111) planes. In Ar-oriented plasma environments, $Cu_3N$ phases were observed, suggesting that oxidation was incomplete, or nitrogen doping occurred. These findings indicate that the HCP-ALD process is extremely sensitive to plasma composition and precursor-plasma interactions.

Hall effect, XPS, and TEM analyses are ongoing to determine the electrical, chemical, and structural properties. This research provides the basis for reliable CuO film growth at low temperature, and future process optimizations are aimed at the production of phase-pure, stoichiometric, and electrically active p-type CuO films.

**TF-ThP-7 Low-Temperature Atomic Layer Deposition of ZnO Thin Films on Cotton for Flexible Electronics***, Habeeb Mousa,* ***Steven Allaby****, Fatih Bayansal,* University of Connecticut*; Md Sazid Bin Sadeque, Tamer Uyar,* Cornell University*; Helena Silva, Necmi Biyikli,* University of Connecticut

The development of flexible electronics has advanced rapidly, with applications from sensors and energy storage to wearables. Among these, photodetectors (PDs) are of growing interest due to their potential roles in health monitoring, security, and optical communication. Zinc Oxide (ZnO), with its wide bandgap, stability under long-term light exposure, and high sensitivity to UV/visible radiation is an ideal material for such devices. However, fabricating thin film-based devices on textiles often affects their mechanical properties such as flexibility, durability, and washability. This work presents an approach that leverages low-temperature atomic layer deposition (ALD) of ZnO on cotton to achieve flexible PDs while preserving the inherent properties of cotton.

ZnO was deposited on cotton (woven bleached, 98 gsm) substrates using diethylzinc (DEZ) and H2O as Zn precursor and co-reactant respectively in a thermal ALD reactor at 120 °C. The unit ALD cycle in which 20 sccm N2 is used as the carrier gas consists of 0.5s DEZ pulse, 30s purge, 0.5s H2O pulse, 30s purge steps. Following the deposition of ZnO layers on cotton, interdigitated electrodes consisting of 200 nm Cr was evaporated by e-beam deposition to create the metal-semiconductor-metal (MSM) structures.

The resulting ZnO films on cotton are characterized in terms of their structural, morphological, compositional, and photo-response properties. X-ray diffraction analysis revealed the polycrystalline nature of the as-grown ZnO layer on cotton. The photo-response characteristics of the fabricated MSM-PD device structures were placed under a solar simulator (Newport 94022A) at a distance of ~20 cm. The bias voltage was scanned from –10 to 10V in a 100-mV step under dark and illuminated conditions. The resulting photo-current at 10V bias showed ~160-fold increase when compared to dark current (from 5.5 nA to 888 nA). Moreover, our study displays an effective ZnO-based photodetector on cotton at low bias voltage of 1V where the photocurrent increased from 0.58 nA to 74 nA (~128 fold increase) highlighting the potential for low-power wearable sensing applications. In order to investigate the sensitivity and stability of the device, the photocurrent—time measurements were conducted by applying five 'ON/OFF' pulses at a bias voltages 10 V. The 'ON' state and 'OFF' state lasted for 5 mins each. The sensitivity was calculated and found to be 271. Future studies could focus on further characterizing the spectral photo-response under various environmental conditions and optimizing the device architecture by exploring different doping strategies, or composite structures that can enhance light absorption.

**TF-ThP-8 The Impact of Bismuth Surfactants on MBE-Grown Insb Thin Films for Applications in Mid-Infrared Devices***,* ***T. Pan Menasuta****, John H. McElearney, Thomas E. Vandervelde,* Tufts University

Indium antimonide (InSb), an important narrow direct bandgap semiconductor (0.17 eV at 300K), is highly optically sensitive in the mid-wave infrared (MWIR, 2-5 µm) spectrum. InSb-based devices are crucial for thermal imaging, spectroscopy, and astronomy as a result of atmospheric transmission and thermal emission characteristics. [1–5]. Its broad sensitivity (1.5-7 µm) also enables gas detection. However, reproducible growth of high-quality InSb epitaxial layers via molecular beam epitaxy (MBE) is challenging due to its low melting point. The epitaxial process requires lower growth temperatures and is prone to crystalline and surface defects. Optimal InSb growth occurs at 385°C with a V: III ratio of 1.2. Accurate temperature control is challenging at these lower temperatures, which further complicates the narrow optimal growth range and can negatively impact the film properties. Controlling surface morphology during growth is critical for advanced optoelectronic devices.

Bismuth surfactancy in MBE has been shown to improve surface morphologies in many III-V materials [6, 7]. A very low bismuth flux can modify the adlayer surface before desorption, and has been shown to improve the morphology of the surface in multiple materials [6–8].To our knowledge, no systematic studies have been reported on the effects of Bi surfactancy on MBE growth of InSb thin films [6, 7, 9]. This study investigates the effects of Bi surfactancy on InSb MBE growth over a wide range of growth temperatures (280-410°C). Two series of homoepitaxial InSb(100) films were grown by MBE: a control set and a set grown with Bi surfactancy, with identical parameters otherwise. The temperature was calibrated using the RHEED pattern transition c(4x4) to a(1x3), which is reported to occur at 370°C [10, 11]. The surface morphology and elemental distribution were analyzed using AFM and SEM-EDS, while XPS confirmed the absence of Bi incorporation. Finally, TEM was performed to analyze the film's lattice structure.

**TF-ThP-9 Strategically Introducing Interfaces into Refractory Concentrated Alloys to Increase Tolerance in Extreme Environments***,* ***Benjamin Derby,*** *Yao Li,* Los Alamos National Laboratory

This work introduces three-dimensional interfaces into refractory concentrated alloys to increase mechanical and conductivity performance in extreme environments. Physical vapor co-deposition at elevated temperature kinetically forces the system to phase separate into alloy architectures with unique 3D interface structures. The increase in dynamic strength and deformability of these structures are tested using a novel high-strain-rate nanoindenter. These materials provide a rapid prototyping framework for developing bulk materials with optimized performance in complex, extreme environments.

**TF-ThP-10 Raman Scattering as a Probe for Tuning Magnetic Quasiparticles in NiO Thin Films Through Ion Beam Irradiation***,* ***Simranjeet Kaur,*** Indian Institute of Technology Delhi, India

NiO is a wide-band transparent insulator, exhibiting a bandgap of 3.6 eV-4.0 eV [1]. It is an antiferromagnetic material with a Néel temperature of 523 K. NiO crystallizes in a NaCl-type face-centered cubic structure with a lattice parameter of 0.417 nm. The antiferromagnetic order in NiO is due to the antiferromagnetic alignment of ferromagnetic (111) planes along the [111] crystallographic direction[2].Below $T_N$,magnetic ordering induces a rhombohedral distortion.This study presents the growth of (111)-oriented NiO thin films on (0001)-sapphire substrate using pulsed laser deposition (PLD). DC magnetic susceptibility measurements of the films confirm that they maintain antiferromagnetic ordering at room temperature. Additionally, this finding is supported by the observation of two-magnon(2M) Raman scattering.The relative intensity of this 2M mode compared to a neighboring phonon mode further highlights the bulk-like antiferromagnetic state in the thin films. NiO thin films were irradiated utilizing an Au ion beam at varying fluences.X-ray diffraction (XRD) analysis indicated a broadening and a shift towards a higher 2θ value in the NiO(111) peak with increased fluence, which suggests a reduction in the out-of-plane lattice parameters.Atomic force microscopy (AFM) results demonstrated increased surface roughness of the films post-irradiation.DC magnetic susceptibility measurements showed a decrease in the magnetic moment and Néel temperature at the higher fluence of $5x10^{12}$ ions/cm$^2$, attributable to defects induced by the ion beam irradiation. Raman spectroscopy further supported these findings, with significant changes observed in the two magnon peaks,which experienced a redshift and broadening in the irradiated samples. This shift and broadening signify a reduced antiferromagnetic coupling due to high-energy ion beam irradiation.Additionally,the 1P peak at 575 cm$^{-1}$ exhibited a redshift and broadening in the irradiated samples. The ratio of $I_{1P}/I_{2P}$ increased significantly upon irradiation and even surpassed one at the higher fluence value, indicating a higher degree of disorder induced by the ion beams. Overall, this study demonstrates the successful deposition of (111)-oriented NiO thin films via PLD, exhibiting magnetic properties similar to bulk NiO, and the tuning of the 2M peak by ion beam irradiation.These findings highlight the potential of NiO thin films for exploring fundamental magnetic interactions and developing optoelectronic applications.

[1]H. Ohta et al., Thin Solid Films 445, 317(2003)

[2]S. M. Rezende et al., J. Appl. Phys. 126, 151101(2019)

**TF-ThP-11 Mesoporous Metal Fluoride Films with Ultra-low Tunable Refractive Index for Broadband Antireflection***, **Choon-Gi Choi**,* Thin Film Materials Research Center, Korea Research Institute of Chemical Technology (KRICT), Republic of Korea*; Dong In Kim, Soonmin Yim, Saewon Kang, Sun Sook Lee,* Korea Research Institute of Chemical Technology (KRICT), Republic of Korea*; Ki-Seok An,* Thin Film Materials Research Center, Korea Research Institute of Chemical Technology (KRICT), Republic of Korea

Porous materials are of great interest in various fields such as optics, biology, energy, and catalysis. While energy and catalysis applications focus on achieving high porosity, optical applications demand not only low-refractive-index (RI) materials that overcome the limitations of naturally occurring substances but also the formation of a smooth RI gradient from the substrate to air. This requires both high porosity and precise control over it. Conventional methods for fabricating porous structures, including templating, self-assembly, and zeolitic synthesis, typically rely on sacrificial templates, which must be removed through chemical etching or thermal treatment, potentially damaging the host material and limiting scalability.

In this study, we present mesoporous metal fluoride films composed of $MgF_2$ and $LaF_3$, fabricated using a simple, template-free, one-step precursor-derived method. Pores spontaneously form during solidification due to the inherent instability of $La(CF_3OO)_3$. Electrostatic interactions between $Mg(CF_3OO)_2$ and $La(CF_3OO)_3$ precursors enable the controlled formation of mesoporous structures with finely tunable RI values ranging from 1.37 to 1.16. By stacking layers of $MgF_2(1–x)–LaF_3(x)$ with different compositions, a graded refractive index (GRIN) antireflection coating (ARC) is achieved, delivering excellent broadband performance with an average transmittance of ~98.03% in the 400–1100 nm range. Despite these advances, a refractive index gap still remains between the fluoride composite and air, primarily due to the inherently high RI of $LaF_3$.

To address this, we propose an innovative approach that enables precise tuning of porosity using micelle-assisted $MgF_2$ precursor intermediates. As micellization increases the size of the $MgF_2$ precursor clusters, the resulting solidified $MgF_2$ grains and the intergranular voids between them also increase, allowing for the fabrication of $MgF_2$ structures with ultra-low RI (~1.04) and fine RI control increments. When applied as a GRIN ARC on quartz substrates, this strategy achieves an average transmittance of ~97.96% across the 250–1100 nm spectral range.

This research was supported by Nano-Material Technology Development Program through the National Research Foundation of Korea (NRF) funded by Ministry of Science and ICT (grant no. 2021M3H4A3A01055854).

**TF-ThP-12 A New Approach to Control Metal Deposition on Dielectrics Selectively Using an Aldehyde Inhibitor***, **Chi Thang Nguyen**, Kailey E. Jones, Jacob Bohreer, Bratin Sengupta, Jeffrey W. Elam,* Argonne National Laboratory, USA

Selective metal deposition on dielectric surfaces (MoD) is essential for advanced microelectronics applications, particularly in the context of the ongoing transition from 2D to 3D device architectures. However, achieving this selectivity remains challenging due to the similar surface chemistries of many dielectrics. In this work, we introduce a new approach for selectively controlling metal deposition on dielectric substrates by area-selective atomic layer deposition (AS-ALD) using an aldehyde inhibitor. Butyraldehyde was employed as an inhibitor to selectively adsorb on and passivate $Al_2O_3$ surfaces while leaving $SiO_2$ surfaces unaffected. As a result, the adsorption of the ruthenium precursor, $[Ru(TMM)(CO)_3]$, was prevented on the aldehyde-inhibited $Al_2O_3$ surface in subsequent Ru ALD cycles and the Ru grew selectively on the $SiO_2$ surface. The inhibitor adsorption behavior, surface blocking properties, and film selectivity were investigated using water contact angle, ellipsometry, scanning electron microscopy (SEM), transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS) measurements. We believe that AS-ALD using aldehyde inhibitors offers a promising pathway for area-selective MoD in general, and for the integration of Ru into complex interconnects and 3D nanoarchitectures in particular, for next-generation microelectronic devices.

**TF-ThP-13 $Al_2O_3$ ALD Mechanism of $Li_6PS_5Cl$: Toward Interface Engineering in Sulfide-Based Solid-State Electrolytes***, **Kyobin Park**, Donghyeon Kang, Vepa Rozyyev, Anil Mane, Francisco Lagunas, Hacksung Kim, Fulya Dogan, Zachary Hood, Peter Zapol, Justin Connell, Jeffrey Elam,* Argonne National Laboratory

Sulfide-based all-solid-state batteries (ASSBs) have emerged as a compelling alternative to conventional Li-ion batteries owing to their superior gravimetric and volumetric energy densities and enhanced safety characteristics. However, sulfide electrolytes such as $Li_6PS_5Cl$ (LPSCl) are prone to chemical and electrochemical degradation upon contact with cathode and anode materials during cycling, giving rise to significant chemo-mechanical instability. Additionally, LPSCl exhibits extreme sensitivity to moisture and air exposure, leading to the release of toxic $H_2S$ gas and the formation of resistive, electrochemically inactive interphases.Atomic layer deposition (ALD) offers a promising strategy to mitigate LPSCl degradation by depositing an ultrathin, conformal buffer layer on the LPSCl that is chemically and electrochemically stable. When properly engineered, this coating not only suppresses interfacial decomposition but can also improve ionic conductivity and mechanical integrity while minimizing electronic conductivity. Despite its potential, the interfacial reaction mechanisms between ALD precursors and LPSCl remain poorly understood.

In this study, we elucidate the reaction mechanism of $Al_2O_3$ ALD using trimethylaluminum (TMA) and $H_2O$ on LPSCl through a combination of in situ and ex situ characterizations supported by density functional theory (DFT) calculations. In situ Fourier transform infrared (FTIR) spectroscopy and ex situ nuclear magnetic resonance (NMR) measurements revealed the surface functional groups involved in TMA chemisorption and subsequent $H_2O$ reactions during the initial ALD cycle. Continued ALD cycling demonstrated steady $Al_2O_3$ growth, as observed by FTIR. Ex situ X-ray photoelectron spectroscopy (XPS) confirmed the formation of new interfacial bonds, while ex situ Raman spectroscopy verified the structural preservation of bulk LPSCl after ALD. Complementary DFT calculations enabled identification of the most thermodynamically favorable reaction pathways for precursor adsorption and film growth.Together, these results provide mechanistic insight into the ALD process on sulfide electrolytes and offer design principles for optimizing interfacial coatings in ASSBs, with implications for broader applications across sulfide-based solid electrolyte systems.

**TF-ThP-14 Controlling the Structural and Electrocatalytic Properties of Pulsed Laser Deposited Ruthenium Oxide thin films for Oxygen Evolution Reactions***, **Jonathan McNair**,* STEM Early College at North Carolina A&T State University*; Russell Boone,* Grimsley High School*; Ikenna Chris-Okoro, Sheilah Cherono, Mengxin Liu, Ghanashyam Gyawali, Veluchamy Palaniappagounder, Shyam Aravamudhan, Dhananjay Kumar,* North Carolina A&T State University

Globally there has been a push for renewable energy sources that can serve in the future as an alternative to the conventional energy sources in existence today that continually lead to environmental degradation. In line with this, research efforts have been geared towards studying the sustainability and reliability of these possible alternatives. In this light, hydrogen generation through the splitting of water is proposed.

This study investigates the electrochemical and structural properties of single crystal ruthenium dioxide ($RuO_2$), focusing on the effect of varying oxidation state (sub-stoichiometric-RuO2-x, stoichiometric RuO2, and hyper-stoichiometric RuO2+x) and lattice strain on electrochemical water splitting particularly in the oxygen evolution reactions (OER) in 0.1M KOH. Electrochemical Impedance Spectroscopy (EIS) and Cyclic Voltammetry (CV) were used to characterize $RuO_2$'s behavior in alkaline environments, extracting key parameters such as solution resistance ($R_s$), charge transfer resistance ($R_{ct}$), and double-layer capacitance ($C_{dl}$). $RuO_2$ thin films were grown through the Pulsed Laser Deposition (PLD) on single-crystal sapphire ($Al_2O_3$) substrates at varying oxygen pressures (25–75 mTorr) at substrate temperatures 600°C at 4800 pulses. Structural characterization was performed using X-ray diffraction (XRD), X-ray Photoelectron spectroscopy (XPS), X-ray absorption spectroscopy (XAS), Non-Rutherford Backscattering Spectrometry (NRBS), Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM). Atomic modelling was carried out using Vesta to understand the epitaxial growth and relationship between the film and substrate. The films' electrochemical performance was evaluated via CV and Linear Sweep Voltammetry (LSV), with emphasis on the effect of crystal structure and oxidation state on OER activity. These results, validate $RuO_2$ as a promising material for water splitting applicationswell as illustrates the importance of deposition ambient control in tailoring the properties of $RuO_2$ film, which is a fundamental part of the design and optimization of an efficient electrode material.

This work was supported by the NSF-PREM on the Collaborative Research and Education in Advanced Materials Center (via grant # DMR-2425119) and the DOE EFRC on the Center for Electrochemical Dynamics and Reactions on Surfaces (CEDARS) via grant # DE-SC0023415.

**TF-ThP-15 Pulsed Laser Deposition and Characterization of Titanium Oxynitride Thin films for Renewable Energy Applications*, Russell Boone,*** Grimsley High School*; Jonathan McNair, Sheilah Cherono, Ikenna Chris-Okoro, Mengxin Liu, Ghanashyam Gyawali, Veluchamy Palaniappagounder, Shyam Aravamudhan, Dhananjay Kumar,* North Carolina A&T State University

In our world today, despite the efforts of various governments and institutions, fossil fuel unfortunately remains the main source of electricity in the United States and globally. These energy sources create toxic emissions, pollute the atmosphere while promoting climate change. In line with the global shift towards developing sustainable fuels, efforts are needed to develop material systems and processes that can convert molecules in the air (e.g., water, carbon dioxide, and nitrogen) into renewable energy products. In response to preventing a continued dependence on fossil fuels, the splitting of water to produce hydrogen fuel and oxygen is proposed.

In this study Pulsed laser deposition (PLD) technique has been used to grow titanium oxynitride (TiNO) thin films on sapphire ($Al_2O_3$) for renewable energy applications. A pulsed Krypton Fluoride (KrF) excimer laser (Wavelength=248nm, pulse duration=30ns) was used, with a laser repetition rate of 10 Hz, 6000 pulses, and a deposition temperature of 600°C.

Structural properties of the films were investigated using X-ray Diffraction and Reflection (XRD, XRR), X-ray Photoelectron Spectroscopy (XPS), Atomic Force Microscopy (AFM) and Scanning Electron Microscopy. Structural modelling was performed using Vesta to understand the epitaxial growth and relationship between the film and substrate.

Electrochemical Impedance Spectroscopy (EIS) and Cyclic Voltammetry (CV) were used to characterize titanium oxynitride (TiNO) behavior in alkaline environments, extracting key parameters such as solution resistance (Rs), charge transfer resistance (Rct), and double-layer capacitance (Cdl).EIS data, analyzed with Nyquist plots and Randles circuit modeling, these results confirmed the presence of both resistive and capacitive elements, validating as a promising material for water splitting applications.

This work was supported by the NSF-PREM on the Collaborative Research and Education in Advanced Materials Center (via grant # DMR-2425119) and the DOE EFRC on the Center for Electrochemical Dynamics and Reactions on Surfaces (CEDARS) via grant # DE-SC0023415.

**TF-ThP-16 Understanding the Electrocatalytic Reaction Kinetics of Ruthenium Dioxide Thin Films using Tafel Equations*, Jonathan Roop,*** *Ghanashyam Gyawali, Mengxin Liu, Sheilah Cherona, Ikenna Chris-Okoro, Wisdom Akande, Brianna Barbee, Veluchamy Palaniappagounder, Shyam Arvamudhan, Dhananjay Kumar,* North Carolina A&T State University

This research focuses on the study of hydrogen and oxygen evolution reaction kinetics of ruthenium dioxide ($RuO_2$) thin films in alkaline and acidic media using Tafel slope analysis. The study has given insights into the rate-determining step, kinetics, and mechanisms that govern electrochemical reactions at the $RuO_2$ electrode and electrolyte interface. The Butler-Volmer equation was also combined with the Tafel equation at higher overpotentials, which has allowed us to establish a connection between the magnitude of the Tafel Slope and the mechanism of the rate-determining step of the reaction. $RuO_2$ is an ideal candidate as an electrocatalyst because it is intrinsically stable, corrosion-resistant, and has low resistivity, making it viable for water splitting applications. The $RuO_2$ films were grown on (0001) plane $Al_2O_3$ under different deposition conditions, using a pulsed laser deposition method. A three-electrode cell and KOH and $HClO_4$ electrolytes with different concentrations were used for Linear Sweep Voltammetry testing. The OER and HER overpotential (h) was plotted as a function of log(j), for which the Tafel slope is calculated using the Tafel equation, h = a + blog(j). For example, Tafel Slope results in 1.0M KOH provide $b_{OER}$ = 115 $mVdec^{-1}$ for the 4800-pulse sample and, $b_{OER}$ = 150 $mVdec^{-1}$ for the 2100-pulse sample. While Tafel Slope results in 0.1M $HClO_4$ provide $b_{HER}$ = 115 $mVdec^{-1}$ for the 4800-pulse sample and, $b_{HER}$ = 160 $mVdec^{-1}$ for the 2100-pulse sample. This data suggests a thicker $RuO_2$ film will result in more kinetic activity on the surface in alkaline and acidic media. Future work will consist of different characterization methods to verify these results and compare our experimental data to theoretical data for further understanding the mechanisms and steps limiting the reactions of $RuO_2$ thin films as a working electrode.

**TF-ThP-17 Crystallinity's Contribution Toward Electrocatalysis of Ruthenium Dioxide Thin Films*, Salil Pai,*** *Ghanashyam Gyawali, Mengxin Liu, Sheilah Cherona, Ikenna Chris-Okoro, Wisdom Akande, Brianna Barbee, Veluchamy Palaniappagounder, Shyam Arvamudhan, Dhananjay Kumar,* North Carolina A&T State University

In this study, high-quality ruthenium dioxide ($RuO_2$) thin films were developed as electrocatalysts, synthesized on sapphire ($Al_2O_3$) substrates via pulsed laser deposition (PLD)—both materials selected for their financial and logistical accessibility. The investigation centered on the relationship between film crystallinity and electrocatalytic performance, comparing two sets of samples: a more crystalline, thicker set deposited with 4800 pulses, and a less crystalline, thinner set deposited with 2100 pulses. Deposition parameters were held constant at a growth rate of 10 pulses per second, a substrate temperature of 600 °C, and a (100) film orientation. Epitaxial growth and crystallinity were assessed through X-ray diffraction/reflectivity, atomic force microscopy, and Hall effect measurements. Electrochemical analysis via the three-probe method revealed a broad potential window with reversible redox behavior, indicating robust electrochemical activity. Charge transfer dynamics were further examined via electrochemical impedance spectroscopy across varying applied potentials and potassium hydroxide concentrations. The thicker, more crystalline films exhibited enhanced performance and long-term stability compared to their thinner, less crystalline counterparts, reinforcing the conclusion that higher crystallinity is critical for electrocatalytic efficiency. These findings underscore the promise of $RuO_2$ thin films as durable, high-performance electrocatalysts for energy conversion and storage, while also motivating future studies to systematically explore how deposition parameters—thickness, temperature, orientation, and growth rate—govern crystallinity and, by extension, catalytic performance.

**TF-ThP-18 Power-Modulated Thermally Assisted Oxygen Plasma for Enhanced Reliability in $Tio_2/Tio_{2-x}$ Memristors*, Beom Gu Lee,*** Chungdaro 1, Republic of Korea*; Jae-Yun Lee,* 409, Chungdaero 1 E8-1, Republic of Korea*; Sung-Jin Kim,* Chungdaro 1, Republic of Korea

The advancement of $TiO_2$-based memristors is critical for next-generation neuromorphic systems and non-volatile memory devices due to their simple structure, scalability, and stable resistive switching properties. However, achieving high endurance and uniform switching remains a major challenge. Precise control of oxygen vacancy distribution is essential to improve device reliability and performance.

In this work, we propose a thermally assisted oxygen plasma process with RF power modulation for the fabrication of glass/ITO/$TiO_2$/$TiO_{2-x}$/Ag memristors. The plasma treatment was conducted at various RF powers (0–80 W) under optimized thermal conditions to investigate its influence on resistive switching endurance, retention stability, and conduction mechanisms. Device performance was evaluated through I–V measurements, endurance cycling, and retention tests.

**Acknowledgements**: This work was supported by Innovative Human Resource Development for Local Intellectualization program through the Institute of Information & Communications Technology Planning &

Evaluation (IITP) grant funded by the Korea government (MSIT) IITP-2025-RS-2020-II201462 (50%), in part by the Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by Ministry of Education under Grant RS-2020-NR049604 (50%)

**TF-ThP-19 Pholuminescence on Room-temperature Germanium-Tin (GeSn)***, **Lia Guo**, Vijay Gregory, Jay Mathews,* University of North Carolina at Charlotte

The use of silicon (Si) in the optics and photonics industry is very popular due to its electronic properties and compatibility with CMOS technology, as well as other semiconductor devices. Germanium (Ge) is an alternative material that can be grown on Si substrates and is now used in photonic devices. However, both Ge and Si suffer from non-radiative processes due to being indirect band-gap materials. Unlike Si, Ge is a quasi-direct bandgap semiconductor and can be band engineered through strain or Sn alloying. Similar to Ge, germanium-tin (GeSn) has shown potential in the photonics industry with a greater focus on light sources. Photoluminescence spectroscopy was carried out using a NIR 980nm laser to probe the optical properties of the GeSn/Ge/Si samples. These measurements were analyzed with reference to Rutherford backscattering and cross-sectional TEM.

## 2D Materials

## Room 208 W - Session 2D+AQS+EM+NS+QS+TF-FrM

## 2D Materials: Devices and Applications

**Moderator: Kai Xiao**, Oak Ridge National Laboratory

8:15am **2D+AQS+EM+NS+QS+TF-FrM-1 Charge Transport in Printed Films of Two-Dimensional Materials for Printed and Wearable Electronics*, Felice Torrisi,*** Imperial College London, UK **INVITED**

Printed electronics has emerged as a pathway for large scale, flexible, and wearable devices[1], Internet-of-Things[2] and smart textiles[3]. Graphene and related two-dimensional (2D) materials offer an ideal platform of novel materials for high performance printed electronics [4,5]. Electronic inks from 2D materials with different electronic properties have been developed to print the different elements of a device: semiconducting or semimetallic inks in the active layer, insulating inks for dielectrics, and conducting inks for electrodes[6].

In this talk I will describe the charge transport mechanisms of surfactant- and solvent-free inkjet-printed thin-film devices of representative few-layer graphene (semi-metal), molybdenum disulphide (MoS2, semiconductor) and titanium carbide MXene (Ti3C2, metal) by investigating the temperature, gate and magnetic field dependencies of their electrical conductivity.[7]

Charge transport in printed few-layer MXene and MoS2 devices is dominated by the intrinsic transport mechanism of the constituent flakes. On the other hand, charge transport in printed few-layer graphene devices is dominated by the transport mechanism between different flakes.[7]

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8:45am **2D+AQS+EM+NS+QS+TF-FrM-3 Antimony as a Contact Material for Two-Dimensional Semiconductors: Interface Chemistry and Thermal Stability***, Fernando Quintero Borbon, Joy Roy, Robert Wallace, **Rafik Addou,*** University of Texas at Dallas

Antimony (Sb), a semimetal, has emerged as a promising contact material for two-dimensional (2D) semiconductors. Sb contacts have been shown to achieve ultra-low contact barriers. The formation of a Sb–Se bond has been demonstrated as an effective doping strategy in n- and p-FETs with a single $WSe_2$ channel through Sb-Pt contact modification. These findings underscore the necessity for further investigation into the interface chemistry and thermal stability of Sb on transition metal dichalcogenides (TMDs), to determine whether the interaction remains van der Waals or becomes chemically reactive upon thermal processing.

The present study offers a comprehensive study of the interface chemistry between Sb and TMDs, in particular $MX_2$ (M = Mo or W; X = S or Se), using X-ray photoelectron spectroscopy (XPS). Sb was deposited in ultra-high vacuum conditions (UHV) on bulk TMD surfaces, followed by annealing in UHV at 100°C, 200°C, and 300°C. The XPS measurements revealed an absence of chemical or interfacial reactions at room temperature, 100°C, and 200°C. However, upon annealing at 300°C, complete sublimation of the Sb layer was observed. These findings support the van der Waals nature of the interface, confirming that the interaction between Sb and the underlying TMDs remains non-reactive up to 200 °C. This thermal stability and inertness suggest that Sb could be a promising candidate for integration in 2D heterostructures and devices that require clean, weakly interacting interfaces.

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9:00am **2D+AQS+EM+NS+QS+TF-FrM-4 Metal-to-Semiconductor Transition in Niobium Sulfoselenide Alloy and Niobium Sulfide Films by Compositional Control and Post Growth Sulfurization*, Tinsae Alem,*** *Abir Hasan, Kory Burns, Nikhil Shukla, Stephen McDonnell,* University of Virginia

Transition metal dichalcogenides (TMD) have attracted increasing scientific interest due to their diverse properties including a tunable bandgap, optical anisotropy, low power consumption, and good elasticity. In this study, low-dimensional TMD films were grown with molecular beam epitaxy (MBE) to investigate the effects of varying chalcogen (sulfur and selenium) content in niobium sulfoselenide ($NbS_xSe_{2-x}$) alloys. Here, we focus on their electrical resistivity and electronic properties, including the transition from metallic to semiconducting behavior to have precise control over the material's electrical conductivity. Additionally, we analyzed the semiconductor-to-metal transition in $NbS_2$ films following post-growth sulfurization and the corresponding changes in resistivity. These MBE grown films were characterized using in-situ x-ray photoelectron spectroscopy (XPS) to analyze the chemical composition. Next, the electrical resistivity of films was calculated using their sheet resistance measured with a Jandel 4-point probe, and their thickness was estimated using x-ray reflectivity (XRR). We used transmission electron microscopy (TEM) to visualize these MBE-grown films at the atomic scale, enabling the correlation of atomic structure with electronic properties. Lastly, the temperature coefficient of resistance (TCR) measurements was performed to understand the resistivity of the films with temperature dependence and to determine their metallic and semiconducting behavior. Our results demonstrate that the transition from metal to semiconductor occurs with the addition of sulfur into the niobium selenide film. We also observed a trend of increasing resistivity as the sulfur content was increased in niobium selenide film. This work explores the potential of tuning the energy gap of TMD materials, making them ideal candidates for tunable nanoelectronics in various applications.

9:15am **2D+AQS+EM+NS+QS+TF-FrM-5 Evolution of the Electronic Gap of Directly Synthesized Versus Mechanically Transferred WS2 Monolayer to Multilayer Films*, Xu He,*** *Antoine Kahn,* Princeton University

Transition metal dichalcogenides (TMDs) have emerged as promising electronics and optoelectronics materials for their strong light-matter interaction, large exciton binding energies, and bandgap tunability through the control of composition and the number of layers. Among TMDs, $WS_2$ stands out for its strong photoluminescence and spin-orbit coupling, making it ideal for exploring charge transfer and interfacial phenomena. However, discrepancies in reported energy levels (electronic gap, ionization energy, electron affinity) remain due to variations in growth and measurement methods, impeding device design.

In this study, we directly compare the band structure of $WS_2$ films from monolayer to multilayer (up to four layers) prepared by two commonly used methods: direct growth via metal-organic chemical vapor deposition (MOCVD) and mechanical exfoliation with layer-by-layer transfer. We utilize a suite of characterization techniques, including Raman spectroscopy, photoluminescence (PL), UV–vis absorption, and X-ray photoelectron spectroscopy (XPS), to probe vibrational modes and optical transitions. A combination of ultraviolet photoelectron spectroscopy (UPS) and inverse photoemission spectroscopy (IPES) allows us to directly study the evolution of ionization energy and electron affinity, hence the electronic gap of the materials.

We find that the electronic gap ($E_g$) of $WS_2$ consistently decreases with increasing layer number, reaching bulk-like values by the trilayer for mechanically transferred layers. The exfoliated monolayer is found to have an $E_g$ of 2.43 eV, which reduces to around 1.97 eV at the trilayer and stays at 1.98 eV for the tetralayer. This layer-dependent $E_g$ reduction is driven firstly by an upshift of the valence band maximum (VBM) at the 1L-2L transition and then by a downshift of the conduction band minimum (CBM) at the 2L-3L transition.

Comparing differently processed layers, we find the MOCVD-gown monolayer $WS_2$ to exhibit an electronic gap of 2.56 eV, larger than 2.43 eV for the mechanically transferred one. The slightly larger $E_g$ in MOCVD-grown monolayers also yields a higher exciton binding energy (~0.55 eV) than in exfoliated monolayers (~0.43 eV). XPS analysis indicates that MOCVD samples contain more oxygen-related defect species, likely contributing to the subtle band gap differences and a small blue shift of their optical spectra relative to exfoliated layers.

Overall, this comparative study highlights the influence of the fabrication methods on the fundamental electronic structure of $WS_2$. These findings provide important guidelines for tailoring band alignments for $WS_2$-based heterostructures and optoelectronic devices.

9:30am **2D+AQS+EM+NS+QS+TF-FrM-6 2D Phase Diagram of Iron Sulfides on Au(111):From Hexagonal to Square Atomic Arrangement and Beyond***, **Andrea Berti**,* University of Trieste, Italy*; Marco Bianchi, Paolo Lacovig, Silvano Lizzit,* Elettra-Sincrotrone Trieste, Italy*; Philip Hofmann,* Aarhus University, Denmark*; Alessandro Baraldi,* University of Trieste, Italy

Despite extensive research on two-dimensional (2D) materials, almost all experimentally synthesized 2D systems derive from van der Waals crystals (vdW). While the use of vdW crystals has been remarkably successful, it inherently restricts the 2D materials landscape to compounds that are already layered in their bulk form. Less than 5% of known inorganic materials possess a layered structure suitable for exfoliation, and the vast majority of functional compounds—such as oxides, sulfides, and nitrides—do not belong to this category. In recent years, increasing efforts have focused on the realization of truly two-dimensional monolayers from non-vdW compounds, which could unlock novel properties in fields such as high-temperature magnetism, catalysis, and strongly correlated electron phenomena. Beyond the class of vdW materials, only a limited number of compounds have so far been theoretically predicted to be stable in the 2D limit. In this context, iron–sulfur compounds have recently emerged as promising candidates. Density functional theory predicts that both hexagonal $FeS_2$ and tetragonal FeS phases can exist as stable monolayers, exhibiting strain-tunable magnetic properties. Although the Mermin-Wagner theorem precludes long-range magnetic order in ideal 2D isotropic systems, magnetic anisotropy can lift this constraint and allow stable ordering, enabling tunable magnetism at the atomic scale, which is essential for spintronics, as well as other emerging phenomena such as topological effects, multiferroicity, and proximity effects in heterostructures. However, compared to their bulk counterparts, Fe–S systems generally display a rich phase diagram, characterized by multiple stoichiometries and atomic arrangements. A similar complexity may also persist in the 2D limit, highlighting the need for a systematic experimental investigation into which 2D $FeS_x$ phases can actually form. For this purpose, we systematically grow and characterize iron sulfide monolayers on Au(111) via in-situ co-deposition of Fe and S. Low-energy electron diffraction (LEED), scanning tunneling microscopy (STM), and X-ray photoelectron spectroscopy (XPS) reveal two primary phases: one with a hexagonal atomic arrangement consistent with $FeS_2$ (Fig. 1a), forming a moiré superstructure, and one with a square arrangement (Fig. 1b). By tuning sulfur exposure, we observe additional phases with varying stoichiometry and atomic arrangement, all belonging to the same 5×5 superstructure family (Fig. 1c). These results confirm the existence of a complex 2D phase diagram for $FeS_x$ monolayers, establishing them as a versatile and tunable platform for exploring 2D magnetism in non-vdW systems.

9:45am **2D+AQS+EM+NS+QS+TF-FrM-7 The Electronic Band Structure and Conduction Band Formation of $HfSe_3$***, **Gauthami Viswan**[1],* University of Nebraska-Lincoln, USA*; Alexey Lipatov,* South Dakota School of Mines and Technology*; Alexander Sinitskii,* University of Nebraska-Lincoln, USA*; Jose Avila,* Synchrotron SOLEIL and Universite Paris-Saclay, France*; Takashi Komesu,* University of Nebraska-Lincoln, USA*; Maria C. Asensio,* Madrid Institute of Materials Science (ICMM), Spain*; Peter A. Dowben,* University of Nebraska-Lincoln, USA

**Abstract:** The anisotropic structure of Group 4 transition metal trichalcogenides (TMTCs) have gained significant interest due to their possible application in optoelectronics. In this work, the band structure of quasi one-dimensional $HfSe_3$ was investigated with nano-spot angle resolved photoemission spectroscopy (nanoARPES). $HfSe_3$ has a rectangular surface Brillouin zone where the effective hole mass along the chain direction is -0.27 $m_{-e}$ which is smaller compared to the effective hole mass along the direction perpendicular to the chains, -1.17 $m_e$. The effective hole mass extracted from the band structure along different high symmetry directions is compared with that of $TiS_3$ and $ZrS_3$ from prior studies.[1] X-ray absorption spectroscopy (XAS) has been used to characterize the unoccupied states of $HfSe_3$ and will be compared to the XAS spectra of $HfS_3$ [2] and $TiS_3$ and $ZrS_3$.[3] The metal chalcogenide hybridization for Hf differs from the Ti and Zr trichalcogenides. This may be due to the increase in effective atomic number leading to strong spin-orbit interaction of Hf based TMTCs.

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10:30am **2D+AQS+EM+NS+QS+TF-FrM-10 Applications of Two-dimensional Materials in Energy, Water, and Healthcare***, **David Estrada**,* Boise State University **INVITED**

The rapidly evolving field of 2-dimensional (2D) materials continues to open new frontiers in fundamental and applied research across water purification, healthcare, and energy applications. This talk will highlight our recent work in the synthesis of 2D and layered-materials-based inks, enabling energy innovations in microsupercapacitors, triboelectric nanogenerators, and electron devices [1-3]. In water applications, we introduce a flowing electrode capacitive deionization (FE-CDI) system utilizing $Ti_3C_2T_x$ MXene electrodes to efficiently remove and recover ammonia from synthetic wastewater and carbonates from simulated ocean water. This FE=CDI system demonstrates promising potential for managing nitrogen and carbon cycles while improving access to clean water [4]. In healthcare, the intersection of graphene and biology offers a powerful avenue for musculoskeletal tissue engineering, where graphene's exceptional physical properties contribute to fundamental biological insights [5-7]. Laslty, this talk will highlight recent insights into $WS_2$ nucleation and film growth on sapphire using tungsten hexacarbonyl and hydrogen sulfide precursors in an AIXTRON 2D Close Coupled Showerhead MOCVD 3 × 2 reactor, with in situ photoreflectometry monitoring.Together, these findings highlight the transformative role of 2D materials beyond graphene in addressing critical engineering challenges and advancing sustainable solutions across diverse fields.

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11:00am **2D+AQS+EM+NS+QS+TF-FrM-12 Electronic Structure Modulation in 2D Metal–Graphene–Metal Electrocatalysts for $CO_2$ Reduction and Hydrogen Evolution Reactions***, **Arturo Medina**, Ines Saih, Vikas Muralidharan,* Georgia Institute of Technology*; Jinwon Cho,* NREL*; Faisal Alamgir,* Georgia Institute of Technology

Two-dimensional metal–graphene–metal (M/Gr/M) heterostructures provide a versatile platform for tuning electrocatalytic behavior through controlled interfacial strain and charge redistribution. In previous work, orbital-level descriptors were introduced to explain how pseudo-epitaxial strain alters the electronic structure of ultrathin metals, driving changes in

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

catalytic activity for the $CO_2$ reduction reaction ($CO_2RR$). These concepts were grounded in density functional theory and validated experimentally by correlating spectroscopic strain signatures with shifts in catalytic onset potential.

Building on this framework, the present study expands the scope and range of electrocatalytic reactions studied in M/Gr/M systems. We integrate new measurements on the hydrogen evolution reaction (HER), exploring whether the same strain–electronic structure–reactivity relationships observed in $CO_2RR$ extend to HER kinetics. This includes analysis of onset potentials, overpotentials, and durability across a diverse set of M/Gr/M configurations. Various metals from the 3d to 5d series were investigated as candidate electrocatalysts, deposited as atomically thin layers on single-layer graphene. The graphene is supported by both metal and metal oxide substrates, enabling systematic modulation of ligand effects and interfacial bonding.

To probe strain and charge transfer, we employ a suite of synchrotron-based and lab-scale techniques including carbon K-edge near-edge X-ray absorption fine structure (NEXAFS), extended X-ray absorption fine structure (EXAFS), ultraviolet photoelectron spectroscopy (UPS), X-ray photoelectron spectroscopy (XPS), and electron energy loss spectroscopy (EELS). We track strain-induced modifications in electronic structure through synchrotron-based spectroscopy, revealing systematic correlations between interfacial bonding, orbital structure, and catalytic performance. By comparing systems with and without graphene, we isolate the role of interfacial bonding in modulating both electronic structure and catalytic behavior.

This work experimentally explores theoretical predictions for HER in M/Gr/M systems and provides new insight into how strain-induced orbital modulation governs charge transfer and reactivity across multiple electrocatalytic reactions. Together, these results highlight M/Gr/M structures as a model system for disentangling the fundamental interactions between dimensionality, strain, and catalytic function.

11:15am **2D+AQS+EM+NS+QS+TF-FrM-13 Large Area Nanostructuring of Van Der Waals Materials for Photon Harvesting in the Flat Optics Regime**, ***Matteo Barelli***[1], *Francesco Buatier de Mongeot, Simone Di Marco,* University of Genoa, Italy*; Rajesh Chennuboina,* University of Genoa, India*; Giorgio Zambito, Giulio Ferrando,* University of Genoa, Italy*; Matteo Gardella,* CNR-IMM, Italy*; Maria Caterina Giordano,* University of Genoa, Italy

2D-Transition Metal Dichalcogenides (2D-TMDs) are two-dimensional semiconductors featuring high optical absorption coefficient combined with good transport and mechanical properties. Although mechanically exfoliated TMDs flakes ensure the best optoelectronic properties, homogeneous large-area growth techniques are mandatory for real-world applications [1,2]. At the same time, in view of light conversion applications in the extreme thickness regime of 2D-TMDs, it is essential to develop effective photon harvesting flat optics strategies derived from nanophotonics.

Here we demonstrate that periodic modulation of few $MoS_2$ and $WS_2$ on large area nanostructured samples fabricated by laser interference lithography (either $MoS_2$ nanostripes arrays or conformal $MoS_2$ layers grown on top of nanogrooved silica templates). These nanopatterned layers can effectively steer light propagation via Rayleigh Anomalies in the flat optics regime, promoting strong in-plane electromagnetic confinement and broadband omnidirectional photon absorption enhancement, with strong impact in photoconversion. [3,4].

As a case study, we investigate the photocatalytic performance of periodically corrugated $MoS_2$ layers for photodissociation of Methylene Blue (MB), a widely used yet harmful textile dye. Under optimized angles coupling light to photonic anomalies, MB degradation is two times faster compared to planar $MoS_2$ films [5]. Additionally, periodic TMD nanostripes serve as directional scatterers, expanding possibilities for advanced light manipulation.

Another major challenge is the scalable fabrication of 2D van der Waals (vdW) heterostructures, often limited to micrometric flakes. Here, we demonstrate large-area ($cm^2$-scale) nanoscale reshaping of vdW heterostructures. Specifically, we report a flat-optics platform using vertically stacked $WS_2$-$MoS_2$ heterostructures endowed with type-II band alignment, forming periodic nanogratings [6]. These engineered large-area vdW heterostructures enable scalable applications in nanophotonics, photoconversion [7], and energy storage.

We recognize founding by the NEST - Network 4 Energy Sustainable Transition - PNRR partnership.

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11:30am **2D+AQS+EM+NS+QS+TF-FrM-14 Exploring the Temperature Coefficient of Frequency (TC*f*) in Graphene Trampoline Resonators**, ***Yunong Wang****, Nawara Tanzee Minim, S M Enamul Hoque Yousuf, Philip Feng,* University of Florida

In this work, we report the first experimental investigation of the temperature coefficient of resonance frequency (TC*f*) in graphene trampoline nanoelectromechanical system (NEMS) resonators. Trampoline resonators are widely used in photothermal sensing applications thanks to their superior thermal isolation, enabling high sensitivities. Leveraging the exceptional mechanical strength, thermal stability, and ultralow mass of two-dimensional (2D) materials, graphene trampoline resonators offer a compelling platform for ultrafast infrared (IR) detection. Characterizing the TC*f* is essential for designing sensors with stable performance across a wide temperature range, enabling high-resolution IR detection, and developing robust NEMS for advanced light sensing applications.

We use focused ion beam (FIB) to make trampoline structure on our graphene drumhead resonator. The resonance characteristics of the device are measured by using a laser interferometry system. An intensity-modulated 405 nm blue laser is employed to drive the device photothermally, and a 633 nm He-Ne laser is used to read out device resonance motions. The reflected light is detected by a photodetector and converted to an electrical signal, which is analyzed by a network analyzer to obtain the resonance response. To measure the resonance frequency at different temperatures, we regulate the temperature of the device with a metal ceramic heater. The temperature of the chip is measured by a platinum resistance temperature sensor.

We measure the resonance response of the device at different temperatures and extract the resonance frequency and quality ($Q$) factor by fitting the measured spectrum to the damped simple harmonic resonator model. The drumhead resonator with 20 μm diameter shows a resonance frequency $f$=3.44 MHz and $Q$=528, while after FIB, the trampoline structure achieves a significantly higher $f$=13.03 MHz and $Q$=5509. As temperature increases, the negative thermal expansion of graphene causes an upward shift in resonance frequency. We observe a TC*f* exceeding 30,100 ppm/°C from the drumhead structure, extracted from frequency shifts between 30 °C and 60 °C. After we FIB the drumhead structure into a trampoline, we found that the TC*f* reduced to 588 ppm/°C.

A lower TC*f* value from the stage heating-up method is desirable for stable operation across varying thermal conditions. Due to geometric isolation and reduced thermal coupling to the substrate, the trampoline is expected to exhibit a smaller TC*f* than its drumhead counterpart. This makes the trampoline resonator a strong candidate for IR sensing applications that require stable performance over a broad range of temperatures.

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[1] **JVST Highlighted Talk**

## Atomic Scale Processing Mini-Symposium
## Room 206 A W - Session AP+EM+PS+TF-FrM

### Area Selective Processing and Patterning

**Moderators: Steven M. George**, University of Colorado at Boulder, **Angelique Raley**, TEL Technology Center, America, LLC

8:15am **AP+EM+PS+TF-FrM-1 Exploring Intermolecular Interactions of an Acetylacetone Variant as Small Molecule Inhibitor for Area-Selective ALD***,* ***Eric Ha Kit Wong****, Marc J. M. Merkx, Joost F. W. Maas,* Eindhoven University of Technology, The Netherlands*; Ilker Tezsevin,* Eindhoven University of Technology, Netherlands*; Wilhelmus M. M. Kessels,* Eindhoven University of Technology, The Netherlands*; Tania E. Sandoval,* Universidad Tecnica Federico Santa Maria, Chile*; Adriaan J. M. Mackus,* Eindhoven University of Technology, The Netherlands

Self-assembled monolayer (SAMs) and small molecule inhibitors (SMIs) are two types of inhibitors for area-selective atomic layer deposition (AS-ALD). One critical requirement for inhibitors is to form densely packed adsorbate layers on the non-growth area. SMIs can be delivered in the vapor phase, which makes them compatible with existing industrial processes. However, the random sequential adsorption of SMIs tend to leave gaps in between the adsorbates (*1*). Intermolecular interactions could improve SMI packing and coverage, potentially leading to a higher selectivity.

π-π interaction is an important class of intermolecular interactions that has been employed in different fields (*2*). To exploit π–π interactions in SMIs, one can introduce aromatic backbones to the molecule. In this work, 3-phenyl-2,4-pentanedione (Hppa (*3*)) is used as the structural variant of acetylacetone (Hacac) for inhibiting ALD on $Al_2O_3$ as the non-growth area over the growth area of $SiO_2$.

Using in–situ reflection–absorption infrared spectroscopy, we examined saturation behaviour, precursor blocking, and thermal desorption of Hppa. The results indicate that Hppa has similar adsorption behaviour as compared to Hacac, in terms of saturation dosages and bonding configurations. Still, various important differences are found: Firstly, the Hppa adsorbates exhibit a transition from a flat-lying configuration at low coverage, to a standing-up configuration at high coverage, suggested by the emergence of the $sp^2$ ν(CH) peak. This indicates that the adsorbates are in orientations that could contribute to π-π interaction. Secondly, the results of blocking tests suggested that Hppa adsorbates are not displaced from the surface by bis(diethylamino)silane (BDEAS) precursor molecules, in contrast to the Hacac case in which ca. 5% of acac adsorbates are removed from the surface by BDEAS. Thirdly, Hppa adsorbates does not show thermal desorption at 150 °C for 10 hours. Instead, the increase in peak area suggest that the adsorbates might undergo rearrangement to other orientations. In summary, our results suggest that the Hppa can be an effective SMI for AS-ALD.

**Reference**

1. J. Li *et al.*, *J. Vac. Sci. Technol. A*. **40**, 062409 (2022).
2. R. Thakuria, N. K. Nath, B. K. Saha, *Crystal Growth & Design*. **19**, 523–528 (2019).
3. O. A. Serra, E. J. Nassar, P. S. Calefi, I. L. V. Rosa, *Journal of Alloys and Compounds*. **275–277**, 838–840 (1998).

8:30am **AP+EM+PS+TF-FrM-2 the Influence of Intermolecular Interaction on the Packing of Small Molecule Inhibitors: A Simulation Study***,* ***Joost Maas****, Marc Merkx,* Eindhoven University of Technology, Netherlands*; Tania Sandoval,* Universidad Tecnica Federico Santa Maria, Chile*; Adrie Mackus,* Eindhoven University of Technology, Netherlands

In recent years, using small molecule inhibitors (SMIs) has become one of the main approaches to achieve area-selective atomic layer deposition (AS-ALD). The main challenge for area-selective deposition (ASD) using SMIs is to obtain a high packing of inhibitor molecules on the surface. Due to the vapor phase dosing, molecules arrive one-by-one at random locations, which leaves gaps in between the inhibitors where potentially a precursor can adsorb, causing loss of selectivity.[1]

In this work we explore the use of attractive intermolecular interactions for achieving higher packing of SMIs via simulations. When employing small molecules, it is expected that van der Waals interactions are too weak to contribute to packing. Consequently, one of the main questions of this work is how strong the interaction has to be to facilitate ordering of molecules on the surface. In addition, the synergy of intermolecular interaction and diffusion of SMIs over the surface is investigated.

The simulation method used for studying the packing of molecules with intermolecular interaction and diffusion is an augmented random sequential adsorption (RSA) model.[1] During every loop of the RSA model, either adsorption or diffusion takes place, based on the adsorption and diffusion rates. The intermolecular interaction energy is implemented in the form of a Metropolis-Hastings algorithm.[2] In the initial work, the molecule is a simple disk on a hexagonal grid with periodic boundary conditions, considering nearest neighboring blocking.

It was found that the coverage of the SMI improves significantly for low diffusion barriers and attractive intermolecular interaction. For interactions energies stronger than approximately -0.15 eV, the formation of domains of higher density on the surface is observed. The results suggest that coverage can be improved significantly by selecting SMIs with sufficient interaction energy and a low diffusion barrier.

1. J. Li; et. al., *JVST A* **2022**, 40 (6), 062409
2. M. Kalos; et. al., *The Annals of Statistics* **1986**, 22 (4), 1701-1762

8:45am **AP+EM+PS+TF-FrM-3 Tuning Surface Reactivity by Small Molecule Modifiers in Area-Selective ALD: Small Molecule Inhibitors (SMI) vs. Small Molecule Promoters (SMP)***,* ***Andrew Teplyakov,*** University of Delaware

In area-selective deposition, selectivity of surfaces could be manipulated to either suppress or promote surface reactivity with respect to the target reactants. Using model ALD processes with $TiO_2$ (TDMAT/water) or $Al_2O_3$ (TMA/water), the deposition onto semiconductor surfaces modified with small fluorine-containing molecules is analyzed by spectroscopic and microscopic techniques, including depth profiling with ToF-SIMS, supplemented by computational DFT modeling. The fluorinated functional groups are designed for easy spectroscopic characterization to analyze the potential AS-ALD schemes on silicon, as well as on oxide materials, including $TiO_2$, MgO, and $Al_2O_3$. The initial deposition steps are analyzed by comparing the behavior of modified surfaces with that of pristine substrates, and the distribution of the fluorine and fluorine-containing fragments within the ALD-deposited layers is followed by ToF-SIMS depth profiling once these F-containing functionalities are buried under the overgrown layers. This approach allows for identification of the deposition processes for both small molecule inhibitors (SMIs) and small molecule promoters (SMPs).

9:00am **AP+EM+PS+TF-FrM-4 Topographically Selective Atomic Layer Etching of $HfO_2$ and $ZrO_2$ Using $NbF_5$ and $TiCl_4$***,* ***Boyun Choi****, Getasew Zewdie, Hyeyoung Shin, Nari Jeon,* Chungnam National University, Republic of Korea

As transistor dimensions continue to shrink, conventional $SiO_2$ gate dielectrics no longer provide adequate capacitance or leakage control, leading to the widespread adoption of high-k oxides such as $HfO_2$ and $ZrO_2$. Yet, achieving atomic-level patterning of these oxides remains a key challenge for advanced device integration. In this study, we investigate their thermal atomic layer etching (ALE) behaviors using $NbF_5$ and $TiCl_4$ as representative halide reactants. A pronounced contrast emerges: $HfO_2$ undergoes smooth, self-limiting etching cycles, whereas $ZrO_2$ exhibits surface roughening and substantial chlorine incorporation. Density functional theory calculations clarify this difference by showing that $TiCl_4$ reacts more aggressively with $ZrO_2$ surface species, destabilizing the surface and degrading etch quality. Extending ALE to nanohole structures with a diameter of 150 nm and a depth of 2000 nm, we further observe topographically selective removal of $HfO_2$. This selectivity is linked to microstructural factors such as crystallinity, indicating that not only chemical reactivity but also structural variations critically influence ALE outcomes. Taken together, these results establish a mechanistic framework for understanding how reactant chemistry and microstructure jointly govern the etching of high-k oxides. Such insights provide practical guidelines for enabling selective integration of $HfO_2$ and $ZrO_2$ in next-generation transistors and interconnect architectures, where atomic-scale precision and material specificity are indispensable.

9:15am **AP+EM+PS+TF-FrM-5 Area Selective ALD for Future Engineering Challenges***,* ***Stacey Bent,*** Stanford University **INVITED**

The continued downscaling of electronic device dimensions requires the development of new, precise patterning methods that are compatible with high-volume manufacturing. Atomic level processing, and in particular area selective atomic layer deposition (AS-ALD), continues to gain attention as an important method to achieve nanoscale features at the sub-10 nm length scale. It is well known that tuning the surface chemistry of the substrate can be used to either inhibit or enhance ALD nucleation, leading to selective deposition. A key strategy for AS-ALD has been the use of inhibitors which can alter the native surface reactivity to block nucleation in thermal as well as plasma-assisted ALD. This inhibition approach enables good selectivity in AS-ALD of thin films on a variety of substrate materials, including dielectrics and metals, and I will present several inhibitor-based AS-ALD systems. Importantly, the ALD precursor also plays a key role in influencing selectivity. Results show that precursor size can have a significant influence on the ability of inhibitors to prevent ALD nucleation. However, precursor size alone is not the defining metric, and I will share examples that highlight the influence of other precursor effects, such as precursor-inhibitor reactivity and miscibility. Ultimately, developing molecular design rules for both inhibitors and ALD precursors will be critical for applying AS-ALD more widely to future challenges in microelectronics fabrication.

9:45am **AP+EM+PS+TF-FrM-7 Controlling ASD of a Multi-Color System: PEDOT ASD between SiN, Si-H, and SiO2 by Pre-Treatment Adjustment***, **Jeremy Thelven**, Nicholas Carroll, Gregory Parsons,* North Carolina State University

Complex 3D device architectures are proposed as the solution to make devices more energy efficient.[1] These architectures require many lithographic steps where the high costs of EUV lithography limits device throughput. As such, there is a need for process augmentation to reduce the EUV burdening. A potential solution is area-selective deposition(ASD), where film deposition occurs on a “growth” surface while it is inhibited on an adjacent “non-growth” surface allowing for bottom-up processing.

While ASD conveys the notion of selective deposition between two surfaces, however, in fabrication more might be exposed. Therefore, it is crucial to look at multiple surfaces, a “multi-color system.” The goal being to have the versatility of depositing the desired material only on the desired location(s). It is then important to know processes that activate or deactivate specific surfaces in a multi-color system.

Poly(3,4-ethylenedioxythiophene)(PEDOT) was deposited by oxidative chemical vapor deposition(oCVD) using 3,4-ethylenedioxythiophene(EDOT) monomer and antimony pentachloride($SbCl_5$) as reactants to analyze how various pre-treatment strategies can tune the ASD between Si-H, SiN, and $SiO_2$ surfaces. As a control, single-material coupons were treated with a diluted hydrofluoric acid(DHF) wet etch prior to PEDOT oCVD. Results showed ~30nm of ASD on SiN and $SiO_2$ vs. Si-H. Three different pre-treatment strategies were evaluated: 1 cycle of molybdenum hexafluoride($MoF_6$)/$N_2$, 7 cycles of N,Ndimethylamino-trimethylsilane(DMATMS)/$N_2$, and 7 cycles of DMATMS/$N_2$ followed by a water soak. Ellipsometer, water contact angle, XPS, and SEM results show that $MoF_6$ served to simultaneously activate and deactivate the Si-H and $SiO_2$, respectively, allowing for PEDOT ASD on SiN and Si-H vs. $SiO_2$. DMATMS exposure deactivated only the $SiO_2$ showing PEDOT ASD on SiN vs. $SiO_2$ and Si-H. Including a water soak after the DMATMS activated the Si-H to PEDOT deposition resulting in a deposition configuration of Si-H and SiN vs. $SiO_2$.

Overall, the concept of tunable selectivity for a three-color system is demonstrated by these results. These pre-treatment strategies providing a better understanding into controlling selectivity.

1.Datta, S.; Chakraborty, W.; Radosavljevic, M. Toward. *Science* **2022**, *378* (6621), 733–740.

10:00am **AP+EM+PS+TF-FrM-8 Kinetics Model for Selective Thermal Etching of $Si_{1-x}Ge_X$ in $F_2$/Ar***, **Yi Chen**, Daniel Cho,* University of California, Los Angeles*; John Hoang, Nicholas Altieri, Ji Zhu, Samantha Tan,* Lam Research Corporation*; Jane Chang,* University of California, Los Angeles

The selective etching of $Si_{1-x}Ge_x$ over Si enables the fabrication of the gate-all-around field-effect transistors. Thermal etching of Si/$Si_{1-x}Ge_x$ at near room temperature features high selectivity, exhibiting a non-linear relationship between etch rate and Ge% (Fig. 1(a)). There are no reported reaction mechanisms explaining this unique Ge%-dependent phenomenon.

In this work, thin films of $Si_{1-x}Ge_x$ of varying Ge content (Ge% = 0 to 1) were etched thermally by molecular $F_2$ gas at near room temperature under different $F_2$ partial pressures (0.5 to 10 mTorr) in Ar. The etch rates were quantified by ellipsometry measurement and the relationship between etch rate and Ge% resembled those shown in Fig. 1(a). Reported $Si_{1-x}Ge_x$ etch selectivity ranges from 100 to 1000 and the unpublished maximum etch selectivity is from 200 to 250. The unpublished experimental data is being reviewed for public release and will be presented at the conference. A kinetics model was established in this work to elucidate the reaction pathways in thermal etching of $Si_{1-x}Ge_x$ by $F_2$, considering reactions between atomic fluorine and various surface species and the interplay between reaction products involving Si and Ge. The model result (Fig. 1(b)) yielded the unique volcano-shaped relationship between etch rate and Ge%, validating the reactions considered in the model captured the main kinetics during $F_2$ etching of $Si_{1-x}Ge_x$.

10:30am **AP+EM+PS+TF-FrM-10 Area-Selective Deposition by Surface Engineering for Applications in Nanoelectronics: Enablement of 2d and 3d Device Scaling and Self-Alignment***, **Silvia Armini**,* IMEC Belgium **INVITED**

At advanced nodes targeting 10 nm feature size and below, lithography starts to dominate costs (EUV, multiple mask passes per layer, pattern placement error,...). Complementary techniques and materials are needed to continue 2D scaling and extend the Moore’s law. On the other hand, 2D scaling is reaching its limitations driving the transition to 3D and vertical integration schemes (such as 3DNAND, 3DDRAM, CFET...), which result in higher devices density per unit area and lower production cost. Area-selective atomic layer deposition (AS-ALD) is rapidly gaining interest because of its potential application in self-aligned fabrication schemes for next-generation nanoelectronics. In addition, ASD allows coping with high aspect ratio and complex 3D architectures. The strong sensitivity of ALD to surface chemistry and its self-limiting nature are particularly appealing for ASD.

In this talk I will illustrate a variety of ASD processes and applications spanning from nano-interconnects, logic and memories to patterning.

11:00am **AP+EM+PS+TF-FrM-12 MO-Mo? Oh No! The Problem of Carbon in Metalorganic Molybdenum Deposition***, **Kyle Blakeney**, David Mandia, Matthew Griffiths, Jeong-Seok Na, Raihan Tarafdar, Jeremie Dalton,* Lam Research Corporation

Molybdenum (Mo) halides and oxyhalides comprise the sole class of precursors that can deposit Mo metal films by ALD/CVD with sufficient purity for applications in advanced microelectronic devices. Unfortunately, solid, low vapor pressure Mo chloride precursors have challenges in flux stability and low vapor pressure. Metalorganic (MO) precursors are commonly used to address some of these challenges and are useful alternatives to halides for many non-metal films such as $SiO_2$, SiN, TiN, $Al_2O_3$, etc. Despite much effort, MO-precursors have not met the performance of chloride precursors for depositing pure Mo.

This presentation will summarize key findings of MO-Mo process development by the Lam ALD/CVD Metals concept and feasibility (C&F) group. Included will be typical precursor tests using coupon process modules, 300mm C&F chambers, fundamental mechanistic investigations of Mo surface reactivity, and novel deposition pathways such as conversion-reduction (Figure 1) and alloy formation (Figure 2).

11:15am **AP+EM+PS+TF-FrM-13 The Effects of Process Chemistry on Blocking Chemisorption in ALD: Thin Film Precursor, Co-Reactant and Co-Adsorbate***, Jay Swarup, James Jensen, Jeffrey Gao, **James Engstrom**,* Cornell University

Achieving area selective deposition requires preventing growth on the non-growth surface (NGS), which often involves the use of molecules to block growth on those surfaces. Careful choice of the ALD process chemistry, thin film precursor and co-reactant, as well as the blocking molecule and how it is administered, is important. We report here a systematic examination of the effects of the precursor, co-reactant and co-adsorbate/blocking molecule on preventing growth of $Al_2O_3$ on $SiO_2$. We also consider the effects of temperature, and the dosing sequence employed for the blocking species. Concerning the precursor we compare trimethylaluminum (TMA) to a non-pyrophoric precursor containing only Al-N bonds and no Al-C bonds, *i.e.*, BDMADA-Al **[1]**. For co-reactants we compare $H_2O$ to *t*-BuOH. Finally, we consider two blocking species: octadecyl trichlorosilane (ODTS), and dimethylamine trimethylsilane (DMATMS). In this study we employ a quartz-crystal microbalance to monitor ALD *in situ* and in real-time, and the deposited thin films have been characterized *ex situ* using X-ray photoelectron spectroscopy, and a variety of techniques. Concerning the “pristine” processes, *i.e.*, ALD in the absence of a blocking molecule, the properties of the films (density, C incorporation, stoichiometry, growth rates) are comparable using either BDMADA-Al or TMA as the precursor under similar reaction conditions. These species also react similarly with $H_2O$ and *t*-BuOH as the co-reactant, where steady growth with the latter is only observed at sufficiently high temperatures. Concerning blocking growth, we have observed a number of identifiable trends. First, employing the same ALD process chemistry, ODTS produces better blocking in comparison to DMATMS in cases involving a single dose of the blocking molecule. When comparing TMA and BDMADA-Al, we observe that for both blocking molecules that the latter is more efficiently blocked. These two observations demonstrate the importance of molecular size as the larger BDMADA-Al is more efficiently blocked, and the larger ODTS is better for preventing growth. Temperature has a definitive effect on the efficiency of preventing growth where we find that higher temperatures lead to more effective blocking of growth. The dosing sequence employed for the blocking species also plays an important role. Repetitive dosing of DMATMS in an "ABC" process provides superior blocking with respect to a single pre-exposure, and these results exceed those produced by ODTS.

[1]J. V. Swarup, H.-R. Chuang, J. T. Jensen, J. Gao, A. L. You and J. R. Engstrom, J. Vac. Sci. Technol. A **43**, 022404 (2025).

## Plasma Science and Technology
## Room 201 ABCD W - Session PS3+TF-FrM

### Plasmas and PVD

**Moderators: Erwin Kessels**, Eindhoven University of Technology, the Netherlands, **Scott Walton**, Naval Research Laboratory

10:45am **PS3+TF-FrM-11 Self-Regulating Electron Temperature in High-Power Impulse Magnetron Sputtering Discharges and Its Effect on the Metal Ion Escape*, Kateryna Barynova,*** University of Iceland*; Nils Brenning,* KTH Royal Institute of Technology, Sweden*; Swetha Suresh Babu,* University of Iceland*; Joel Fischer, Daniel Lundin,* Linköping University, Sweden*; Michael A. Raadu,* KTH Royal Institute of Technology, Sweden*; Jon Tomas Gudmundsson,* University of Iceland*; Martin Rudolph,* Leibniz Institute of Surface Engineering (IOM), Germany

We analyze how the primary electron temperature in high-power impulse magnetron sputtering (HiPIMS) depends on the sputtered target. The analysis is based on the experimental discharge data for 7 different target materials, which were modeled using the Ionization Region Model (IRM), a semi-empirical global model for HiPIMS discharges. We observe that the electron heating and collisional cooling processes stabilize after some time into the pulse (20 - 40 µs) reaching a steady state and leading to an almost constant electron temperature; the initial transients in the electron temperature are caused by only small discrepancies in these terms. The underlying mechanism that causes this self-regulation are the rate coefficients for electron impact ionization, which increase monotonically with electron temperature. This leads to a self-balancing mechanism in which an increase in the electron temperature increases the collisional losses of the kinetic energy of electrons because of the higher collisions rate with species in the ionization region. The opposite is true for the decreasing electron temperature. In addition, the steady-state electron temperature depends on the target material and inversely correlates with the self-sputter yield of the target. The species composition in the ionization region shifts from being composed of argon species to target species; and argon has a much higher ionization potential compared to all the studied target materials, so both the ionization and cooling rates substantially increase only at the higher electron temperatures compared to the ionization region composed of target species. This explains the experimentally observed low electron temperature in high self-sputter yield target discharges. Since the mean free path of the sputtered atoms, before being ionized, depends on the electron temperature, we can explain with the IRM results why in metal-rich discharges ionization occurs further away from the target, leading to higher chances of ionized sputtered species to escape to the substrate because the electric field is weaker there. The dominating species in the ionization region, which define the main collisional loss process and the electron temperature, are not identified only by the sputter yield of the target, but by a more complex recycling loop of argon and target species in the ionization region and the rarefaction of argon in front of the target.

11:00am **PS3+TF-FrM-12 Comparison of Particle Size and Morphology of Graphene-Like Carbon Grown with and Without Substrate in Atmospheric Pressure Microwave Plasma*, Parker Hays,*** *Dhruval Patel, Dren Qerimi,* University of Illinois at Urbana-Champaign*; Michael Stowell,* Lyten*; David Ruzic,* University of Illinois at Urbana-Champaign

Graphene-like carbon materials were synthesized on a substrate as well as free-standing using an atmospheric pressure microwave plasma (APP) system. Argon and nitrogen were utilized as carrier gases and methane as the carbon precursor. This study compares the morphological and structural differences of the materials formed under each growth condition.

Free-standing carbon material was collected from the APP using quickly inserted TEM grids at various distances from the microwave insertion point. Carbon was also grown on a temperature-controlled aluminum surface using the same APP system by placement of the aluminum substrate at different distances from the microwave insertion point.

Scanning Electron Microscopy (SEM) images were used to find the particle diameter distributions for each case, showing for both the free-standing carbon and the carbon grown on aluminum that mean primary particle size increased as a function of increased methane flow rate and distance from the microwave insertion point, and decreased with an increase in microwave forward power. Furthermore, the particle diameter distributions in the free-standing case showed minimal change past the bulk plasma boundary, meaning most of the free-standing graphene growth occurred in the bulk plasma and at the boundary.

Raman spectroscopy was employed to evaluate the structural order and defect density of the carbon materials. The free-standing material exhibited a higher $I_D/I_G$ intensity ratio, suggesting increased disorder and a more amorphous structure compared to substrate-grown samples, which displayed sharper G and 2D peaks indicative of more crystalline graphene. These findings suggest that while substrate-free growth at atmospheric pressure offers a more scalable and simple synthesis route, growth on substrate may yield higher structural quality in the resulting carbon materials.

11:15am **PS3+TF-FrM-13 Mass Spectrometric Study of Ar-Diluted Ammonia Borane Plasma for H-Bn 2d Film Formation*, Takeshi Kitajima,*** *Reiji Kawasaki, Toshiki Nakano,* National Defense Academy, Japan

Ammonia borane is used as a relatively safe source of BN for the rapid synthesis of h-BN, an important insulating material[1] in the field of two-dimensional electronics[2]. Ammonia borane plasma attracts attention when aiming at high-speed film formation, and analysis of active species in the plasma is necessary. In this study, active species generated from ammonia borane powder irradiated with Ar plasma were analyzed by mass spectrometry.Parallel plate type 100MHz driven capacitively coupled plasma generated in a high vacuum chamber is used. After placing 0.1 g of ammonia borane ($BH_3NH_3$) powder on the RF electrode and evacuating, a 10 W glow discharge was formed with an Ar gas flow rate of 30 sccm. A copper sample heated to 800°C was placed downstream, and when BN radicals were supplied at a pressure of 800 Pa, an h-BN atomic film was formed over 30 minutes as shown in the SEM image and Raman spectrum of Fig. 1(a,b). Radical analysis in the downtream was performed with a mass spectrometer at a pressure of 30 Pa. Figure 1(c) shows the difference in the mass spectrum when the plasma is turned on and off. $BNH_5$(30) is increased by plasma lighting. $O_2$(32) is produced by plasma irradiation to the chamber wall.Radicals generated from ammonia borane raw material leading to formation of h-BN atomic film are presumed to be $BNH_5$ generated by decomposition of $BH_3NH_3$. Dangling bonds of BNH5 are thought to generate chemical reaction activity on the substrate.Time dependence of mass signal is shown in Fig.1(d). The relation of OH and $BNH_5$ is shown in Fig.1(e). OH is linearly related to $BNH_5$ amount and presumed to the major source of production. Contrally, O signal is nonlinear to the $BNH_5$ signal as shown in Fig.1(f). The consequence of the oxygen related radical exposure will be summarised in the presentation. 1 K.H. Lee, et.al. Nano Letters 12, 714 (2012).2 L. Song, et.al. Nano Letters 10, 3209 (2010).

11:30am **PS3+TF-FrM-14 Automated Deposition Chamber for Functional Dielectrics: Development and Implementation*, Stanislav Udovenko,*** *Ian Mercer, Susan Trolier-McKinstry, Jon-Paul Maria, Darren Pagan,* The Pennsylvania State University

S. A. Udovenko[1], I. Mercer[1], S. Trolier-McKinstry[1], J. P. Maria[1] and D. C. Pagan[1]

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**Automated Deposition Chamber for Functional Dielectrics: Development and Implementation**

The dielectric and piezoelectric properties of ferroelectrics make them essential in the fabrication of multilayer ceramic capacitors (MLCCs) and various transducers (such as those used in medical ultrasound, naval sonar, and consumer electronics) [1–3]. Modern devices demand high-quality, reproducible material synthesis, especially in the fabrication of complex multilayer structures where the thickness of individual layers critically affects device performance. In this context, automating the material synthesis process becomes highly beneficial, as it reduces human error, increases repeatability, and improves overall efficiency. However, there is currently a disconnect between university-based materials design and synthesis which is primarily an analog process and large-scale automated manufacturing found in industry.

This project focuses on developing a framework for digitizing and automating functional ferroelectric synthesis in a university setting. Our demonstration case is the sputtering of ferroelectric films within a vacuum deposition chamber. In the initial stage, a data acquisition and controller system was designed and installed on deposition chamber automized for doped AlN. Next, LabVIEW-based software was developed to acquire data from all electronic units of the chamber—including sputter cathode power supplies, mass flow controllers, temperature controllers, and vacuum pumps. Following software development, control functionality was implemented, enabling the system to send control commands to all electronic units while simultaneously logging process parameters in real time. Additionally, Python scripts were developed to convert deposition recipes—originally created in Microsoft Excel—into system control routines, easing use by non-experts.

**References:**

[1] Jaffe, B., Cook, W. R., & Jaffe, H. (1971). *Piezoelectric Ceramics*. Academic Press.
[2] Setter, N., et al. (2006). "Ferroelectric thin films: Review of materials, properties, and applications." *Journal of Applied Physics*, 100(5), 051606.
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## Thin Films
## Room 206 B W - Session TF-FrM
## Fundamentals of Thin Films III

**Moderators: Mark Losego**, Georgia Institute of Technology, **Junjie Zhao**, Zhejiang University

8:30am **TF-FrM-2 Themally-Managed QCM in ALD for Rapid Saturation Curves*, David Kane,*** Arradiance LLC

Optimizing atomic layer deposition (ALD) processes can require many saturation curves and days of time. In any process, the deposition temperature, precursor doses, and often at least one precursor temperature need to be selected, often by preparing saturation curves. A quartz crystal microbalance (QCM) can significantly accelerate this process by enabling saturation curves to be collected quickly, but QCM is very temperature-sensitive and can produce incorrect results. Indeed, many researchers reject QCM for this reason.

This work demonstrates several strategies for using QCM, overcoming the challenges of its thermal sensitivity. The frequency vs temperature profiles of commercially available quartz crystals are compared. Thermal isolation and gas load impacts are explored to minimize variations in the QCM temperature. With good thermal stability, it was possible to produce multi-parameter 3D saturation curves to rapidly optimize ALD process parameters.

8:45am **TF-FrM-3 Conductive Transparent Porous Al-Doped ZnO Conformal Coatings Synthesized Using Sequential Infiltration Synthesis Method*, Vasanta Gurung,*** *Diana Berman,* University of North Texas

In this study we demonstrated a simple approach for the fabrication of conductive, transparent, nanoporous, and conformal aluminum-doped zinc oxide (AZO) coating using sequential infiltration synthesis (SIS) method. Block copolymer (BCP) polystyrene-block-polyvinyl pyridine (PS-b-P4VP) was employed as a polymer template for infiltrating metal-oxide precursors, leading to the synthesis of nanoporous AZO coatings. We show that both the porosity and electrical conductivity of the AZO coatings could be precisely tuned by swelling the polymer template in a suitable solvent and adjusting the number of SIS cycles. We achieved up to 80% porosity, with a low aluminum-to-zinc doping ratio of 1:17, resulting in a resistivity of approximately 7.83 Ωcm, as measured using conductive atomic force microscopy (C-AFM) and Hall effect measurements. Additionally, the AZO coating exhibited average transmittance of over 80%, confirming its high transparency. These results highlight a highly effective and reliable method for synthesizing conductive, transparent, nanoporous, and conformal AZO coatings, which exhibits a promising potential for a wide range of optoelectronic applications.

**KEYWORDS:***sequential infiltration synthesis, block copolymer, aluminum-doped zinc oxide, conductivity*

9:00am **TF-FrM-4 Effect of Aminosilane Precursor and Initial Surface Silanol Density on O2 Plasma-Assisted ALD of SiO2*, Andrew Kaye,*** Colorado School of Mines*; Bhushan Zopé,* Intermolecular, Inc.*; Xinjian Lei, Agnes Derecskei, Haripin Chandra,* EMD Electronics, USA*; Sumit Agarwal,* Colorado School of Mines

$SiO_2$ is a commonly used dielectric material in semiconductor manufacturing, and aminosilanes are typically used as the Si precursor during radical-assisted atomic layer deposition (ALD) of $SiO_2$. This work explores the role of the initial surface Si−OH density, the substrate temperature, and the structure of the aminosilane precursor on the growth per cycle (GPC) for ALD on plasma-deposited $SiO_2$ substrates. Specifically, we studied $O_2$-plasma-assisted ALD of $SiO_2$ using two aminosilanes, di-*sec*-butylaminosilane (DSBAS) and dimethylamino trimethylsilane (DMATMS). The surface reactions during ALD were monitored using *in situ* attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy, and the GPC was monitored using *in situ* four-wavelength ellipsometry. On an $SiO_2$ surface with a high initial Si−OH group density, *in situ* ATR-FTIR spectroscopy shows that ~30% more Si−OH groups are consumed by DMATMS than DSBAS because DSBAS contains a bulkier amino leaving group than DMATMS. *In situ* ellipsometry shows that at an ALD temperature of 100 °C, the GPC using DSBAS and DMATMS are ~1.8 and ~1.2 Å, respectively. The higher GPC for DSBAS shows that the initial aminosilane coverage does not influence the GPC. We speculate that during the $O_2$ plasma step, O radicals can easily insert into Si−H bonds in adsorbed DSBAS. However, for adsorbed DMATMS, surface $Si-(CH_3)_3$ groups must be combusted, and then converted to Si−OH groups from species generated in the $O_2$ plasma.

On an $SiO_2$ surface with a low initial Si−OH group density, approximately the same number of Si−OH groups react with DMATMS and DSBAS. Therefore, we conclude that once the initial surface Si−OH density is sufficiently low, steric effects do not play a role in initial aminosilane adsorption on $SiO_2$. For both DMATMS and DSBAS, at a constant ALD temperature, the initial $SiO_2$ surface Si−OH group density has no effect on the GPC of $SiO_2$ ALD. *In situ* ellipsometry shows that on an $SiO_2$ surface with a low initial Si−OH group density, no nucleation delay is observed compared to a film with a high initial Si−OH group density. This implies that more Si−OH groups are produced during the first few $O_2$-plasma half-cycles compared to the initial density of adsorbed aminosilanes on the surface, allowing steady-state ALD to be reached within 5 ALD cycles. As ALD temperature for DSBAS increases, the GPC decreases. This is due to the thermal instability of reactive surface groups such as Si−OH and Si−H, and the areal density of these sites decreases with increasing temperature.

9:15am **TF-FrM-5 Low-Temperature Growth of Epitaxial III-Nitride Films via Hollow Cathode Plasma Atomic Layer Deposition*, Steven Allaby,*** *Habeeb Mousa, Fatih Bayansal, Abiodun Aderibigbe, Mustafa Yavuz, Steven Suib, Helena Silva, Necmi Biyikli,* University of Connecticut

The III-nitride compound semiconductor family plays a critical role in optoelectronic devices and transistor channel materials, particularly for high-power and high-frequency applications. In this study, AlN, GaN, and InN thin films were deposited on c-plane sapphire and n-Si(111) substrates via hollow cathode plasma atomic layer deposition (HCP-ALD). Trimethylaluminum (TMA) was used as the aluminum precursor; triethylgallium (TEG) for gallium; and trimethylindium (TMI) for indium. N2 and H2 plasma were included for AlN and GaN, while N2 was included for InN. For each III-nitride film, the effect of adding argon to the plasma gas composition was investigated. All film depositions took place under 100W rf-power and at a substrate temperature of 200°C.

The resulting films were characterized using ellipsometry, x-ray diffraction (XRD), ultraviolet-visible spectroscopy (UV-Vis), and scanning transmission electron microscopy (STEM) imaging. In situ ellipsometry showed linear growth in AlN; accelerated growth in GaN; and delayed growth in InN. The growth per cycle (GPC) values were obtained as 1.21, 0.45, and 1.10 Å for AlN, GaN, and InN, respectively. Spectroscopic ellipsometry showed an increase in refractive index when Ar was included for AlN and InN, while refractive index decreased when Ar was included for GaN. XRD patterns showed highly crystalline films oriented along the (002) plane. Ar inclusion resulted in an increase in the (002) peak for GaN and InN films, while it reduced the (002) peak for AlN. From UV-Vis and Tauc analysis, the optical bandgaps were obtained as 5.80, 3.22, and 1.96 eV for AlN, GaN, and InN, respectively. High-angle annular dark-field (HAADF) STEM images showed monocrystalline films for AlN and GaN, forming smooth interfaces with sapphire. InN appeared polycrystalline with distinct grain boundaries.

Future work involves characterizing the electrical properties of III-nitride films, performing Hall effect measurements to obtain conductivity type, carrier concentration, and mobility. X-ray photoelectron spectroscopy will be performed to determine the amount of carbon and oxygen impurities in the films. After optimizing InN and GaN, InGaN will be alloyed under similar conditions to enable bandgap engineering.

This work contributes to the development of stable and reliable n-type nitride semiconductors for back-end-of-line (BEOL) transistor channel materials.

9:30am **TF-FrM-6 Understanding Oxygen Evolution Reaction and Charge Transfer Behavior at the Electrode-Electrolyte Interface Using Pulsed Laser-Deposited Ruthenium Oxide Thin Films***, **Mengxin Liu,*** North Carolina A&T State University

Ruthenium oxide ($RuO_2$), regarded as one of the benchmarks for oxygen evolution reaction electrocatalyst materials during water splitting, has been grown in epitaxial thin film form using a pulsed laser deposition method. The precision in the $RuO_2$ thin films structure, surface orientation, and oxygen stoichiometry have been investigated using high-resolution structural characterization techniques that include x-ray diffraction, x-ray reflectometry, Raman Spectroscopy, and x-ray photoelectron spectroscopy. Following the structural characterization, the films were subjected to four-probe resistivity and Hall measurements via the Van der Pauw method and electrochemical measurements via a three-electrode system. The control in the $RuO_2$ thin film surface orientation was realized using high-quality single crystal rutile Titanium oxide ($TiO_2$) substrates with (100), (101), and (110) orientations. Due to different atomic arrangements of Ru and O atoms and interatomic orbital positions in these planes, these films profoundly differ in electrical resistivity, charge carrier density, and dominance in the nature of charge carriers, hence, in the net electrochemical properties. The electrochemical measurements and analysis carried out on the $RuO_2$ thin film with (101) orientation displays the highest electrochemical current density and the lowest onset potential among the $RuO_2$ films with other orientations. The next part of our study has focused on understanding the role of oxygen defects in $RuO_2$ thin films in their electrochemical properties. For this purpose, $RuO_2$ thin films were on $TiO_2$ substrates with (110) orientation at substrate temperatures of 500, 600, and 700 °C. After the deposition was over, all the films were cooled to room temperature from the deposition temperature in two hours under the high vacuum conditions of $2\text{-}3\times10^{-6}$ Torr. The x-ray photoelectron spectroscopy results carried out on these films have shown that the binding energy center of the corresponding Ru3d doublet peaks for the 700 °C sample is 0.5 eV lower than for the 500 and 600 °C samples. These results indicate the formation of oxygen vacancies with the variation of Ru oxidation states near the top surface of the thin film. According to the electrochemical measurement, the 700 °C sample displays the lowest overpotential (500 mV) at the current density of 10 $mA/cm^2$ and also the lowest Tafel slope (101.6 mV/dec) than others. Additionally, the electrochemical double larger capacitance of the deposited thin films, measured by different methods, indicates that the 700 °C has the highest value of 61.20 µF, compared with the 26.87 and 28.35 µF for 500 and 600 ° samples, respectively.

9:45am **TF-FrM-7 Growth of Ag Nanomorphologies by High-Temperature Glancing Angle Deposition — from Initial Growth Stage to Whisker/Plate Formation***, **Motofumi Suzuki,*** Kyoto University, Japan*; Khushi Aggarwal,* Indian Institute of Technology Delhi, India*; Ayako Miki, Taisei Morita, Kota Saeki, Taichi Banno, Kyoko Namura,* Kyoto University, Japan

It is known that high-temperature glancing angle deposition (HT-GLAD), where vapor is deposited at an angle greater than 80° from the substrate normal onto a substrate heated to a temperature exceeding one-third of the melting point of the evaporated material, can induce whisker growth in metals such as Al, Cu, Ag, Au, Mn, Fe, Co, Ni, Ti, and Zn. These whiskers can have diameters ranging from several tens to several hundreds of nanometers and lengths of several micrometers or more [1]. Among these metals, the morphologies of Al [2] and Fe [3] have been studied in detail concerning substrate temperature and deposition amount. However, the mechanisms of nucleation and the development of complex morphologies remain unclear.

In this presentation, we will report on the results of investigating the HT-GLAD of Ag at higher substrate temperatures than previously reported.

The Si substrate was introduced into the vacuum chamber, evacuated to the $10^{-5}$ Pa range, and then heated to a temperature between 500 °C and 625 °C. A tungsten (W) basket, serving as the evaporation source, was positioned at an angle of 83° from the substrate normal. Approximately 1 g of Ag grains were loaded into the W basket, and evaporation commenced after the substrate temperature had stabilized. The deposition amount was monitored using a quartz crystal thickness monitor, and was converted to a average thickness of 10-60 nm.

At a substrate temperature of 500 °C, no significant structures were observed at a deposition amount of 10 nm. However, when the deposition amount exceeded 20 nm, numerous particles and whiskers with diameters of less than 100 nm grew on the surface. Additionally, platelets, which had not been observed in conventional HT-GLAD, were found to grow with their wide surfaces facing the incident direction of the Ag vapor.

In the presentation, we will discuss the effects of substrate temperature and materials on the growth mechanism of Ag nanomorphology.

[1] M. Suzuki et al.: Jpn. J. Appl. Phys. 52 (2013) 110116.

[2] M. Suzuki et al.: J. Vac. Sci. Technol. A 25 (2007) 1098.

[3] M. Suzuki et al.: Proc. SPIE 7041 (2008) 70410H.

10:00am **TF-FrM-8 Controlled Growth of Tellurium Network Structures for Multi-Spectral Photodetector Applications***, **Ahmed Adel A. Abdelazeez,** Wanseok Oh, Yizhou Wang, Tom Schmedake, Yong Zhang, Haitao Zhang,* University of North Carolina at Charlotte

Recently, tellurium (Te) has gained significant interest for its unique helical atomic chain structure bonded by van der Waals (vdW) forces. It exhibits thickness-dependent electronic properties similarly to two-dimensional (2D) materials, along with strong spin–orbital coupling from its chiral structure and enhanced environmental stability. As a p-type semiconductor, Te has a narrow band gap (1.2 to 0.3 eV), large responsivity, high detectivity, high on/off ratios, and high carrier mobility, making it a promising material for short-wavelength infrared (SWIR) photodetection. Although a convenient physical vapor deposition (PVD) has been widely applied as a tailored growth technique for the Te growth, the critical parameters controlling the synthesis of 2D and 1D Te structures remain unclear. Herein, this research focuses on understanding the growth mechanism of Te nano- and microstructures. Key parameters, such as pressure, temperature, and growth time, have been systematically explored to study their effects on growth evolution. Various Te structures, including microspheres, microrods, microplates, nanowires, etc., have been synthesized at different growth zones. This study makes it possible to realize controlled growth of different Te structures and a research focus is centered on a unique Te network structure of microrods (Te-Net). This innovative structure is the first of its kind to be reported, as previous reports have mostly been focused on individual micro- or nanostructure. The network structure enables low-cost device fabrication without sophisticated lithography.

The Te-Net based photodetectors demonstrate excellent responsivity (R) and detectivity (D*) under different illumination conditions, with typical values as high as R = 0.43 A/W and D* $=3.98 \times 10^7$ Jones at 405 nm. At 532 nm and 808 nm, the device exhibits responsivity of $8.6 \times 10^{-3}$ A/W and $7.3 \times 10^{-3}$ A/W, and detectivity of $9.6 \times 10^5$ Jones and $7.4 \times 10^5$ Jones, respectively. We are investigating the photoresponse mechanisms including direct carrier photogeneration and local heating for further performance improvement. One important phenomenon we discovered is that the devices are extremely sensitive to the dark environment with the room lights off. No significant visible/near-infrared light was detected from the dark environment using a commercial spectrometer and no existing theory explains this phenomenon. Therefore, future research will focus on investigating the source of the light signals and the mechanism of this extreme sensitivity. We are looking into the device performance under illumination of other light sources, especially those in the SWIR to mid-wavelength infrared ranges

10:30am **TF-FrM-10 A Comparative Study of Effects of Ultraviolet Irradiation and Laser Curing on Hydrogenated Amorphous Carbon Thin Films***, **Md. Mahfujur Rahman**, Rajib Chowdhury, Seonhee Jang,* University of Louisiana

Hydrogenated amorphous carbon (a-C:H) materials can be utilized in a variety of applications, mainly as protective, wear-resistant, or anti-reflective coatings for optical windows. The a-C:H materials show distinct material properties, such as high density, hardness, chemical inertness, and electrical resistivity. The fabricated a-C:H materials are often subjected to a post-processing to enhance optical and physical properties such as refractive index, extinction coefficient, optical bandgap, and surface roughness. For the post-processing of the a-C:H materials, ultraviolet (UV) irradiation and laser curing are considered. In this study, the a-C:H films deposited by plasma-enhanced chemical vapor deposition (PECVD) method underwent the UV irradiation or laser curing, and the effects of these post-processing treatments on the a-C:H thin films were investigated and compared. First, the a-C:H films were deposited on Si (100) substrates by PECVD using cyclohexane ($C_6H_{12}$) precursor at room temperature with a plasma power of 80 W. The pristine films exhibited characteristics of being optically transparent, hydrophobic, and topologically smooth.

For UV irradiation, the a-C:H thin films were exposed to a 255 nm light source in air. The UV irradiances were 2.2 and 16.5 mW/cm$^2$, respectively, and irradiation times were 1 and 4 hours. For laser curing, the a-C:H films were exposed to Nd:YAG laser source. The Nd:YAG laser had a wavelength of 1064 nm, a pulse duration of 4 ns, and a pulse rate of 3.75 Hz. The laser fluences were 100 and 400 mJ/cm$^2$, respectively. The a-C:H films were characterized using Fourier-transform infrared spectroscopy (FTIR), ellipsometry, contact angle geometry, and atomic force microscopy (AFM) to identify chemical bonding structure, optical properties, wettability, and surface morphology, respectively.

UV irradiation reduced the film thickness due to surface ablation. Despite the changes in thickness, the films were optically transparent with a smooth surface topology. Additionally, while the optical bandgap decreased, the wettability of the films increased substantially. Hydrogen depletion and oxygen incorporation were confirmed by characterizing the films with FTIR. On the contrary, the post-processing laser cured films did not show a significant change in thickness but exhibited an even smoother surface compared to pristine films. FTIR analysis showed an improved sp$^3$ bonding network and a reduced graphitic sp$^2$ content. In conclusion, this comparative study highlights the significance of selecting an appropriate curing method based on specific application requirements.

10:45am **TF-FrM-11 Synthesis, Characterization, and Classification of Polymer-Like Hydrogenated Amorphous Carbon**, ***Seonhee Jang***, *Rajib Chowdhury, Thomas Poché,* University of Louisiana at Lafayette

Hydrogenated amorphous carbon (a-C:H) films exhibit a wide range of properties that depend on the hydrogen (H) content and the hybridization of their carbon (C) atoms as sp$^3$, sp$^2$, or sp bonded. The a-C:H films with high sp$^3$ content offer high hardness, chemical inertness, and electrical resistivity. These properties enable the a-C:H films to apply for hardmask, diffusion barrier, sensors, protective coatings, and biocompatible films. Graphite-like a-C:H films with high sp$^2$ content show increased conductivity and a reduced optical bandgap. This study focuses on polymer-like a-C:H films with a varying H content of 40–50%, leading to a low-density, soft matrix with reduced cross-linking. Additionally, their friction coefficient is also influenced by H, promoting a lubricating transfer layer. This study explores their structural characteristics, emphasizing their potential applications and differences from other a-C:H subclasses.

The a-C:H thin films were deposited by plasma-enhanced chemical vapor deposition (PECVD) of a cyclohexane ($C_6H_{12}$) precursor. The effects of deposition parameters such as reactor pressure and plasma power on the characteristics of the polymer-like a-C:H films were investigated. For the first set of the a-C:H films, the deposition plasma power of 80W supplied from the RF power generator was fixed, and the deposition pressure varied from 19.73 to 38.00 Pa. For the second set of the a-C:H films, the pressure was maintained between 19.73 and 20.93 Pa, and the deposition plasma powers were 20, 40, 60, and 80 W. The optical, and chemical properties of the a-C:H materials were analyzed using various characterization tools such as spectroscopic ellipsometry, atomic force microscopy, Fourier transform infrared (FTIR) spectroscopy

Through these analyses, the a-C:H materials were determined to be optically transparent, topologically smooth, and hydrophobic in nature. The refractive index and FTIR spectra of the films were consistent with those of polymer-like a-C:H. The a-C:H films had optical bandgaps ranging from 3.09 to 3.69 eV, classifying them as wide-bandgap semiconductors. The materials deposited at higher plasma powers and lower pressures were found to have an increased refractive index, which is known to correlate with density. The relative H content of the a-C:H films displayed an inverse relationship with the refractive index, suggesting that H within the films inhibits cross-linking and reduces the density. These results indicate that the formation of more energetic plasma at higher plasma powers and lower pressures results in a-C:H films with a reduced H content and increased density.

11:00am **TF-FrM-12 Pulsed Laser Deposition of Bulk-Like NiO Thin Films**, ***Simranjeet Kaur***, Indian Institute of Technology Delhi, India

Nickel oxide (NiO) is a wide-bandgap transparent insulator with a band gap ranging from 3.6 eV to 4.0 eV. It is an antiferromagnetic material with the Néel temperature of 523 K, which is much larger than the room temperature. It exhibits NaCl-type face-centered cubic crystal structure with the lattice parameter of 0.417 nm. The antiferromagnetic order of NiO is associated with the antiferromagnetic alignment of the ferromagnetic (111) planes along the [111] direction. A rhombohedral distortion develops in the structure below Neel's temperature. Here, we report the growth of (111)- and (001)-oriented NiO thin films on (0001)-Sapphire and (001)-MgO substrates using pulsed laser deposition (PLD), respectively. The DC magnetic susceptibility of the films (~120 nm) confirms that the films are antiferromagnetic at room temperature. We further proved this by showing two-magnon Raman scattering response from the films down to at least 30 nm in thickness at room temperature. We studied the optical properties of the samples using UV-vis, ellipsometry, and photoluminescence spectroscopy. In particular, we obtained the band gap of x eV, which is well within the range expected for bulk NiO. For photoluminescence measurements, we excited NiO(111)/$Al_2O_3$(0001) film at the wavelength of x nm, and obtained the two bands at 385nm and 405nm, respectively. The signature of exciton-magnon coupling is obtained, as the linewidth of the peak at 405nm increases with decreasing temperature, which indicates the presence of exciton-magnon coupling. Overall, our study demonstrated the pulsed laser deposition of (001)- and (111)-oriented NiO films that have bulk-like magnetic and optical properties.

11:15am **TF-FrM-13 Evaluating Repeatability of Structural and Electrical Properties of PLZT Films Prepared Using Three Distinct Sol-Gel Routes**, ***Sneha Kothapally***, *Sushma Kotru,* The University of Alabama

The sol-gel method, a widely used chemical solution deposition technique, offers precise control over stoichiometry and chemical composition, low processing temperatures and low fabrication cost without the need for high vacuum environment. Owing to these advantages, sol-gel method has become a preferred route for fabricating ferroelectric materials such as Lead Lanthanum Zirconate Titanate (PLZT) thin films. However, the film properties are highly influenced by the method of preparation of solution (Sol) and achieving repeatable results remains a major challenge limiting their use in practical applications. In this study, three different sol-gel preparation methods adopted from literature were employed to prepare PLZT sols. Each sol was used to fabricate films resulting in a total of three sets of samples. These films were systematically analyzed for their structural and ferroelectric properties to evaluate the impact of solution preparation method on the film performance. One representative sample from each set was further subjected to detailed surface and compositional analysis using scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), and X-ray photoelectron spectroscopy (XPS). The primary objective of this work was to assess the repeatability of properties within each set and identify the sol preparation method that yields the most consistent and optimal properties. Comparative findings from all three solution methodologies will be presented and discussed.

# Author Index

## Bold page numbers indicate presenter

# Author Index

# Author Index

# Author Index

# Author Index