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 5x10^{-7} to 1x10^{-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$_3$As$_2$ 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.

[1] Denis R. Candido, Michael E. Flatté, and J. Carlos Egues. Blurring the boundaries between topological and nontopological phenomena in dots. Phys. Rev. Lett., 121:256804, Dec 2018.

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[3] M. Marcinkiewicz, S. Ruffenach, S. S. Krishtopenko, A. M. Kadykov, C. Consejo, D. B. But, W. Desrat, W. Knap, J. Torres, A. V. Ikonnikov, K. E. Spirin, S. V. Morozov, V. I. Gavrilenko, N. N. Mikhailov, S. A. Dvoretskii, and F. Teppe. Temperature-driven single-valley Dirac fermions in HgTe quantum wells. Phys. Rev. B, 96:035405, Jul 2017.

[4] K. Y. Ma, Z. M. Fang, R. M. Cohen, and G. B. Stringfellow. Organometallic vapor-phase epitaxy growth and characterization of Bi-containing III/V alloys. Journal of Applied Physics, 68(9):4586–4591, 11 1990.

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$_x$Te$_{1-x}$/CdTe devices with vapor transport technology (VTD) and characterized the structural chemistry and electronic properties of CdSe$_x$Te$_{1-x}$/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$_x$Te$_{1-x}$/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$_x$Te$_{1-x}$/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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[3] T. Stevenson, D. G. Martin, P.I. Cowin, A. Blumfield, A. J. Bell, T. P. Domyn, P. M. Wearver, Piezoelectric materials for high temperatures transducers and actuators, J. Matter. Scpi. Mater Electron 26, 9256-9267, 2015.

[4] M. Demartom Maeder, D. Damjanovic and N. Setter, Lead free piezoelectric materials, J. of Electro ceramics, 12, 385-392, 2004.

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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 ºC for 8.5 minutes. The TiO_2 provides a source of electron conduction (2.2 x 10^{-7} S/cm) and the NASICON-type LTP provides a source of fast Li-ion conduction (9.3 x 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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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 ($^2F_{5/2} \rightarrow ^2F_{7/2}$) 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.

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**

Electronic Materials and Photonics
Room 207 A W - Session EM2+AIML+AP+CPS+MS+SM-TuA

Advances in AI and Machine Learning within the Semiconducting Industry

Moderator: Erica Douglas, Sandia National Laboratories

4:00pm **EM2+AIML+AP+CPS+MS+SM-TuA-8 Improved Design-of-Experiments and Process Modeling with Generative AI*, Somilkumar Rathi,*** *Muthiah Annamalai,* Panmo LLC

Small volume semiconductor, photonic and materials manufacturing largely uses One-Factor at-a time (OFAT) to discover process window instead Design of Experiments (DOE). We demonstrate, *Panmo Confab,* a Generative AI based DOE and process-flow-design platform to accelerate process window discovery. Large volume semiconductor, photonic and materials automation tools have relied on statistical process control (SPC), design of experiments (DOE) and yield modeling techniques which are fairly manual and depend on specialized tools and deep knowledge [1,2]when such tools are not used we get a sub-optimal outcomes for process development teams through using one-factor at a time (OFAT). In this article we report, and demonstrate, *Panmo Confab* a Generative AI based process flow tracking and design of experiments platform to accelerate flow designs and generating DOEs. Previously our tool was used without Generative AI, features to show improvement in process discovery for plasmonic nanocavity fabrication [4]. The unique innovation of our tool is to use the emerging technology of large language models (LLM), like BERT or ChatGPT [5,6] and science of causality [3] to enable generation of process flows with a description. Our tool is presented in both on-premises and Software-as-a-Service (SaaS) formats.

References:

1. Montgomery, D. C. Design and analysis of experiments. (John Wiley & sons, 2017).

2. May, G. S., & Spanos, C. J. Fundamentals of semiconductor manufacturing and process control. (John Wiley & Sons, 2006).

3. Pearl, Judea, and Dana Mackenzie. The book of why: the new science of cause and effect. (Basic books, 2018).

4. Annamalai, M., Rathi, S., Methodology for robust process window discovery in plasmonic nanostructures", Proc. SPIE 13111, Plasmonics: Design, Materials, Fabrication, Characterization, and Applications XXII, 131110A (2024).

4:15pm **EM2+AIML+AP+CPS+MS+SM-TuA-9 Foundation Models in Semiconductor R&D: A Study on Segment Anything*, Fei Zhou,*** Sandisk Corporation

Quantitative analysis of scanning and tunneling electron images is crucial in semiconductor manufacturing, particularly for defect detection, process margin checking, and morphology quantification. Traditional AI/ML approaches, such as using recurrent neural networks, require large labeled datasets and extensive transfer learning to generalize across different imaging conditions. Developing a usable AI tool for proof-of-concept demonstrations demands significant engineering effort and GPU resources, making these methods costly and time-consuming. These challenges are especially pronounced in semiconductor R&D, where fast turnaround, high accuracy, and efficient use of engineering resources are essential.

The Segment Anything Model (SAM) introduces a novel training free segmentation approach, eliminating the need for task-specific retraining while providing robust and efficient segmentation across diverse semiconductor imaging requirements. This paper explores SAM's application in semiconductor image analysis, demonstrating its ability to segment complex nanoscale features without prior dataset exposure. We assess SAM's performance in automated defect detection, where challenges such as varying defect morphology, background noise, and process-induced variations exist. With appropriate prompting and post-processing techniques, SAM adapts to different imaging conditions, offering a rapid, low-cost, and high-accuracy solution.

Additionally, we examine SAM's limitations, particularly in scenarios where the region of interest is small and contains limited useful pixel data. By employing image enhancement techniques, we demonstrate how SAM can effectively segment defects even in low-information conditions. Furthermore, we explore how integrating grounding techniques with SAM can expedite segmentation post-processing, further improving efficiency in real-world applications.

Our case studies show that SAM significantly reduces resource overhead and enables semiconductor image analysis automation, achieving saving of >100 engineering hours and >20 GPU hours per project. Its foundation model architecture allows it to generalize across different defect types, backgrounds, and imaging techniques without additional data labeling or fine-tuning. These findings suggest that integrating SAM into semiconductor workflows enhances efficiency, lowers costs, and accelerates R&D decision-making by providing a scalable and cost-effective solution for high-precision image segmentation. This study highlights the transformative potential of foundation models in semiconductor engineering, paving the way for broader adoption of AI-driven automation across the industry.

4:30pm **EM2+AIML+AP+CPS+MS+SM-TuA-10 MOFCreatioNN: A Novel Modular Machine Learning Approach for Designing 'Undesignable' Metal-Organic Frameworks.*, Satya Kokonda,*** Charter School of Wilmington

Many critical material discovery processes remain too complex for traditional computational modeling, necessitating costly and time-intensive experimentation. Here, we present a generalizable, application-driven methodology for material design, demonstrated through a case study in photocatalysis. Using a reinforcement learning ensemble, we generated 120,000 novel metal-organic frameworks (MOFs) optimized for CO_2 heat of adsorption and CO_2/H_2O selectivity. A multi-objective fitness function—incorporating stability, catalytic potential, cost, sustainability, and adsorption properties—enabled computational modeling of photocatalytic performance aligned with industrial criteria. To enhance efficiency and prevent feature overfitting, a predictor funnel system iteratively filtered low-scoring candidates, narrowing the search space to 17,315 MOFs and improving computational efficiency by 313%. Our system, MOFCreatioNN, designed two high-performing, de novo MOFs: a Cr-based MOF with a photocatalyst score 239% higher than the control, and a Mn-based MOF that outperformed all baselines across every evaluated metric, demonstrating robustness against imperfect fitness functions. The proposed MOFs meet key synthesis and operational thresholds—including X-ray diffraction consistency with known structures, predicted synthesizability, temperature stability >300°F, and viable water stability—making them practical for real-world applications. Furthermore, we identify actionable design heuristics, such as the significant impact of the N_262 metal cluster on photocatalytic performance. By integrating industrial considerations such as cost, stability, and environmental viability into the modeling process, this work showcases a scalable framework for the AI-driven design of industrially relevant materials in domains previously considered computationally intractable.

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 β-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 β-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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[1] S. J. Pearton, F. Ren, M. Tadjer, and J. Kim. J. Appl. Phys. **124**, 220901 (2018).

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

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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3.Zhou, M. *et al. J. Mater. Chem.* **5**, 1247–1254 (2017).

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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.

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 $\pm V\text{-}_{max}$ 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 $\pm V\text{-}_{max}$ 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 $cm^2V^{-1}s^{-1}$. 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 $cm^2V^{-1}s^{-1}$, 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 $cm^2V^{-1}s^{-1}$. 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 (Vmax), 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

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[1] **JVST Highlighted Talk**

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 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.

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:

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[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
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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_2O 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_2O 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_2O 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.

Electronic Materials and Photonics
Room 205 ABCD W - Session EM-ThM

Advances in Material Deposition Techniques

Moderators: Francois Fabreguette, Micron, **John Muth**, North Carolina State University

8:45am **EM-ThM-4 Unveiling the Synergy of Er_2O_3 and Mxene for Efficient and Durable Energy Storage Systems***, **M.R. Ambika,*** Ramaiah institute of Technology, India

MXenes, a rapidly expanding family of two-dimensional transition metal carbides and/or nitrides, have sparked intense scientific interest due to their unique combination of metallic conductivity, tunable surface chemistry, and hydrophilic behavior (surface area=15.247 m^2 g^{-1}). These properties not only make them ideal candidates for standalone electrode materials but also allow seamless integration with other functional compounds to form high-performance composites. In this study, a hybrid material was designed by coupling Ti_3C_2 MXene with Erbium oxide (Er_2O_3), a rare-earth metal oxide known for its redox-active behavior, to engineer a next-generation electrode for energy storage devices. The layered Ti_3C_2 sheets were synthesized via selective chemical etching, followed by hydrothermal composite formation with Er_2O_3. The structural, morphological, and chemical characteristics of the resulting materials were thoroughly analyzed using XRD, FESEM, FTIR, and Raman spectroscopy. The hybrid system demonstrated a striking enhancement in electrochemical performance due to the synergistic interplay between the high conductivity of MXene and the faradaic contribution from Er_2O_3. The pure MXene electrode delivered a specific capacitance of 476.19 F g^{-1}, while the optimized MXene/Er_2O_3 composite achieved a high capacitance. In addition, there was an improvement in cycling stability (85.99%) of the composite when compared to MXene (77.4%) for 2000 cycles. This remarkable improvement underscores the potential of rare-earth metal oxide/MXene hybrids in advancing the design of efficient, high-capacity energy storage systems. The work opens new avenues for tailoring MXene-based architectures toward scalable, high-performance energy storage and conversion technologies.

9:00am **EM-ThM-5 The CO_x Thermal Oxidation Process for CO_2 Capture***, **Marshall Buffett,*** Voiland School on Chemical Engineering

Rising carbon dioxide emissions have driven research into sustainable methods for converting carbon rich waste gases from industry into value-added materials. One such method is the CO_x Thermal Oxidation Process (CO-OP), in which CO or CO_2 reacts with magnesium silicide (Mg_2Si) to produce crystalline silicon encapsulated in both graphitic and amorphous carbon. The resulting composite shows potential as a lithium-ion battery anode, while the process itself offers a method for CO_2 removal. However, industrial gas streams are rarely pure and the influence of feed composition on CO-OP remains unexplored. While CO-OP with CO_2 has been studied, implementation in industrial processes would be impractical if it required purified CO_2. This study investigates how feed compositions common in methane steam reforming (CO_2, CO, CO+H_2, and CO_2+H_2) affect the morphology of the produced composite and how these morphology changes influence battery performance. Preliminary results indicate that CO increases the carbon content of the composite as compared to CO_2 and creates a core/shell structure, increasing mechanical stability. Morphology, surface area, and carbon distribution vary significantly with gas composition which in turn affects the battery performance significantly. X-ray diffraction confirms high purity across all samples after leaching. These insights guide future improvement of CO-OP for integration with industrial emission streams, creating a new method of carbon capture and improving battery technology.

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_3interlayers 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

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

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

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.

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 SrTiO₃ 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 ~2×10^{17} cm^{-3} to ~1×10^{20} cm^{-3}, achieving Hall mobilities from ~300 $cm^2/(V\cdot s)$ up to over 50,000 $cm^2/(V\cdot s)$ 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.

12:00pm **TF+CPS+MS+EM-ThM-17 Examining the Spin Structure of Altermagnet MnTe Epilayers Grown by Molecular Beam Epitaxy***, **Qihua Zhang**[2],* 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 ~7.5×10^{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] **AVS Graduate Research Awardee**

[2] **TFD Distinguished Technologist Award**

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 4.3cm^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)

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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.

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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.

Electronic Materials and Photonics
Room Ballroom BC - Session EM-ThP

Electronic Materials and Photonics Poster Session

EM-ThP-1 Comparison of Experimental Analysis and Theoretical Calculation of the Lattice Dynamics, Phonon and Vibrational Spectra Dynamics of Titanium Nitride and Oxynitride*, Ikenna Chris-Okoro*, *Sheilah Cherono, Wisdom Akande, Swapnil Nalawade, Mengxin Liu, Barbee Brianna, Brooklyn Jenkins, Ghanashyam Gyawali, Bishnu Bastakoti, Shyam Aravamudhan, J. David Schall, Dhananjay Kumar,* North Carolina A&T State University

Titanium nitride (TiN) and its isostructural oxide derivative, Titanium oxynitride (TiNO) has gained interest in industry as a cost-effective alternative material to noble metals and refractory metals with wide range of applications especially in the optoelectronics and plasmonic. However, there still remain some gaps and disagreement in the literature on specific optical and photoelectrochemical properties of TiN and TiNO, due to difficulty and the varying approach in quantifying defects, vacancies, oxidation state and direct impact of impurities in experimental results.

In this study, thin films of TiN and TiNO were synthesized via pulse laser deposition on sapphire. Structural properties of these thin films were investigated using X-ray Diffraction and Reflection (XRD, XRR), X-ray Photoelectron Spectroscopy (XPS), Rutherford backscattering spectrometry (RBS), Raman Spectroscopy and Fourier Transform Infrared Spectroscopy (FTIR). To corroborate our experimental observations, the phonon dispersions and Raman active modes are calculated using the virtual crystal approximation for rutile TiO_2 and rocksalt TiNO and molecular dynamics simulations were used to calculate the phonon density of states. The results shows that the incorporation of nitrogen atoms does not significantly alter the phonon dispersions of rutile TiO_2. However, it results in the emergence of new phonon modes at approximately 7.128 THz (237.65 cm^{-1}) at the Gamma point, which corresponds to the experimentally observed Multi-Photon Phase-MPP (240 cm-^{1}-R). From the experimental and theoretical studies, a multilayer optical model has been proposed for the TiN/TiNO epitaxial thin films for obtaining individual complex dielectric functions from which many other optical parameters can be calculated.

This work was supported by a DOE EFRC on the Center for Electrochemical Dynamics and Reactions on Surfaces (CEDARS) via grant # DE-SC0023415. Part of the work has used resources established by the Center for Collaborative Research and Education in Advanced Materials (CREAM) via NSF PREM grant # DMR-425119 PREM.ML and GG are jointly supported by the CEDARS and CREAM projects.

EM-ThP-2 Reliability Improvement for Nanostructured High Power AlGaAs/GaAs Vertical-Cavity Surface-Emitting Semiconductor Lasers*, Gwomei Wu,* Chang Gung University, Taiwan

The objective of this study has been to develop high power 850 nm vertical-cavity surface-emitting laser (VCSEL) using oxidation confinement technique. The active layer consisted of three pairs of $Al_{0.3}Ga_{0.7}As$/GaAs semiconductor nanostructures and it exhibited a photoluminance emission wavelength of 835 nm. Distributed Bragg reflector mirror nanostructures of 40 pairs in n-type and 21 pairs in p-type were designed to confine the resonance. The multi-layered epitaxial wafers were further processed by photolithography techniques. Inductively coupled plasma etching was employed to create the platform during the mesa process. Various non-oxidized aperture sizes have been achieved by a wet-oxidation method. The experimental results showed that the VCSEL device exhibited low threshold current of 0.6-0.8 mA. The optical output power was about 6.0-6.8 mW at the injection current of 6 mA. The slope of efficiency was found to be about 3.2~3.7 mW/mA. The corresponding voltage was in the range of 1.7~2.1 V. On the other hand, an eye diagram could be clearly observed under the high data rate of 25 Gbit/sec. The response frequency was measured at 17.1 GHz at -3 dB, also at the injection current of 6 mA. In addition, a high thermal conducting AlN (~230 W/m-K) dielectric bonding substrate was employed to improve device reliability. The related electro-optical characteristics would be presented and further discussed.

EM-ThP-3 Singlet Fission from Tetracene and Charge Transfer to Metal Halide Perovskites*, Yutong Ren*[1], *Antoine Kahn,* Princeton University

Metal halide perovskites (HaPs) have garnered widespread interest for light-harvesting and light-emitting applications due to their exceptional optoelectronic properties and relatively simple fabrication methods. However, like with other semiconductors, HaP-based solar cells lose excess energy through thermalization when absorbing photons with energy that exceeds the absorber bandgap.[1] A promising strategy to reduce these losses and improve photon utilization is to exploit singlet fission, whereby a high-energy singlet exciton formed in an adjacent layer splits into two triplet excitons.[2,3] By transferring these triplet excitons into a HaP film engineered with a composition that aligns the absorber's bandgap closely with the exciton energy, one can effectively harvest this otherwise wasted energy. In our work, we demonstrate that singlet fission in the molecular semiconductor tetracene (Tc) efficiently generates triplet excitons[4] that are energetically matched to the bandgap of a Sn–Pb based HaP, offering a viable pathway toward improved device performance.

In this study, we investigate the electronic structure of Sn–Pb-based HaP films and their interfaces with Tc using ultraviolet photoelectron spectroscopy (UPS) and inverse photoemission spectroscopy (IPES). Based on the work by Nagaya et al.,[5] we introduce a second molecular donor, zinc phthalocyanine (ZnPc), at the interface to engineer a more staggered energy alignment between Tc and the perovskite film, thereby promoting an energetically more favorable sequential electron transfer plus formation of a charge transfer (CT) state ($ZnPc^+$ - HaP^-). UPS/IPES measurements suggests that the CT state lies approximately between the Tc triplet energy and the HaPenergy gap, which is favorable for triplet transfer. Complementary photoluminescence (PL) and time-resolved PL (tr-PL) measurements provide guidance for selecting alternative donors with deeper or shallower HOMO levels to replace ZnPc and further refine the interfacial energetics. Moreover, optoelectronic characterization reveals insights into undesirable charge carrier recombination pathways at the organic/HaP interface. Collectively, our results underscore the potential of singlet fission to enhance the efficiency of perovskite solar cells and reduce the cost of the energy that they generate.

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EM-ThP-6 Title:Plasma-Enhanced ALD of Phase-Tunable Ternary Oxynitrides for Bandgap-Engineered Charge-Selective Contacts in Perovskite Photovoltaics*, George Kwesi Asare,* University of Science and Technlogy, Republic of Korea

We introduce a PE-ALD route for depositing aluminum-zinc oxynitride (AZON) films using alternating pulses of triethylaluminum (TEAl), diethylzinc (DEZ), oxygen plasma, and N_2/H_2 remote plasma. By precisely controlling the oxygen-to-nitrogen incorporation ratio during deposition at, we achieve continuous tuning of the AZON bandgap enable tailored alignment with both valence and conduction bands of the novel material.

In-depth structural and compositional analyses using spectroscopic ellipsometry, Rutherford backscattering (RBS), and grazing incidence X-ray diffraction (GIXRD) confirm that ALD-grown AZON films exhibit uniform density, amorphous character, and atomically sharp interfaces. Ultraviolet photoelectron spectroscopy (UPS) and in situ Kelvin probe measurements reveal controlled shifts in the work function of over 0.8 eV, enabling their application as either electron or hole transport layers depending on the ALD cycle ratio and post-deposition annealing. When incorporated as an electron transport interlayer, between the perovskite and the hole transport layer, AZON-enhanced devices exhibit a stabilized power conversion efficiency (PCE) of 23.8% with negligible hysteresis and retain over 91% of initial performance after 1500 h under continuous 1 Sun illumination. Furthermore, thermally accelerated aging tests reveal suppressed ion migration at the interface, attributed to the passivating nature of the nitrogen-rich surface.

The integration of conformal, compositionally tunable charge-selective layers remains a challenge in advancing the long-term stability and interfacial energetics of next-generation perovskite solar cells (PSCs). In this

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[1] **JVST Highlighted Poster**

work, we report a novel application of plasma-enhanced atomic layer deposition (PE-ALD) to synthesize ternary metal oxynitride (M–O–N) thin films with phase-tunable electronic properties for use as hole and electron selective interlayers for PSC applications.

EM-ThP-7 Growth of $MAPbI_3$ Single Crystals for Radiation Detection and Sensor Applications*, **Basak Bagci**, Shams Noor, Ge Yang,* North Carolina State University

Hybrid halide perovskites such as methylammonium lead iodide ($MAPbI_3$) offer exceptional promise for ionizing radiation detection due to their high atomic number, strong photon absorption, low trap densities (~10^{10} cm^{-3})and excellent defect tolerance. In particular, single-crystal $MAPbI_3$ stands out for its excellent charge transport properties, including high mobility–lifetime (μτ) products ~1.2 × 10^{-2} cm^2/V and X-ray sensitivities exceeding 250 μC Gy^{-1} cm^{-2}, which are critical for achieving high-sensitivity, low-noise performance in X-ray and gamma-ray detectors.

This study focuses on the growth of $MAPbI_3$ single crystals dissolving methylammonium iodide (MAI) and lead iodide (PbI_2) in gamma-butyrolactone (GBL), followed by controlled heating to induce crystal formation. Experimental efforts will explore the effects of precursor concentration, temperature ramp rates, and growth dynamics on crystal size, morphology, and electronic characteristics. Theharvested crystals are intended for use in radiation detection and broader sensor applications, and they will also serve as a baseline for future comparisons with triple-cation and doped perovskite systems.

Our work builds on previous ITC reports but demonstrates a new synthesis protocol that yields centimeter-scale $MAPbI_3$ crystals with low visible defect density and improved reproducibility. Unlike earlier studies, our method carefully regulates supersaturation and convection to promote steady lateral crystal expansion. Preliminary optical and structural analyses confirm phase purity and high crystallinity, while ongoing electrical characterization is focused on quantifying μτ values under bias and assessing detector sensitivityand leakage currentunder X-ray flux. To address the well-known stability limitations of $MAPbI_3$, we are implementing post-growth annealing strategies, encapsulation and/or low-temperature storage under inert conditions to suppress decomposition. These steps aim to improve the operational durability of the material and establish a foundation for stable detector integration.

By establishing a reliable and reproducible synthesis and growth protocol, this work aims to produce high-purity, low-defect $MAPbI_3$ crystals suitable for device integration. Future steps include evaluating charge transport characteristics, assessing detector performance under radiation exposure, and exploring strategies for enhancing long-term material and device stability. The insights gained from this study are expected to contribute to the development of scalable, low-cost perovskite-based radiation detectors with improved resolution and sensitivity.

EM-ThP-8 Chemical Vapor Deposition of Uniform and Large-Scale MoS2 Using Heterogeneous Precursor*, **Xiaokai Zhu**,* Duke University*; Gang Seob Jung,* Oak Ridge National Laboratory*; Jiahui Yang,* Duke University*; Xuguo Zhou,* Boston College*; Zhe Shi,* Massachusetts Institute of Technology*; Victoria Ravel, Chung-Li Lin, Xingjian Hu, Zihan Peng, Aaron Franklin,* Duke University*; Qiong Ma,* Boston College*; Tania Roy, Haozhe Wang,* Duke University

The mass production of large-scale single-layer molybdenum disulfides (MoS_2) is necessary for the fabrication of next-generation electronics. However, the current chemical vapor deposition (CVD) strategies are hard to produce uniform and large-scale single-layer MoS_2. Here, we developed a CVD strategy using heterogenous precursors for synthesizing high-quality single-layer MoS_2. Different from the traditional CVD strategies where the growth promoter and Mo source are mixed, our strategy employs heterogeneous precursors where the growth promoter and Mo source are positioned separately in two layers. During heating, the growth promoter initially volatilizes and condenses on the substrate to create a promoter-rich environment. In that case, a large amount of promoter accumulates and spreads uniformly on the substrate, leading to the growth of millimeter-scale single-layer MoS_2 on both SiO_2/Si and sapphire substrates. Raman spectroscopy and atomic force microscopy (AFM) imaging have confirmed the MoS_2 layer number. Raman and photoluminescence (PL) mapping indicated outstanding spatial uniformity of the film. Selected-area electron diffraction revealed single crystal properties within a 5 μm × 5 μm area. An array of field-effect transistors based on the as-grown single-layer MoS_2 demonstrated excellent electrical properties (10E-7 on/off ratio). Compared to traditional CVD strategies, the coverage ratio of single-layer MoS_2 increased from 66.7% to 90.3%, and the device yields increased from 6.0% to 74.0%. The growth mechanism was investigated by density functional theory (DFT) calculations concluding that the energy barrier for MoS_2 growth on salt is significantly lower. As a result, after the growth of the first layer, no additional layers tend to grow on top of it and all single-layer flakes merge together to form a continuous film with multiple domains which have been visualized by second harmonic generation (SHG) imaging and molecular dynamics (MD) simulation. This method provides a new understanding of the mechanism of the promoting agent in CVD MoS_2 growth, presents a new paradigm for high-quality MoS_2 fabrication, and consequently will benefit large-scale 2D semiconductor applications.

EM-ThP-9 Comprehensive Study of Tandem Cdsete Photovoltaic Devices Using Alternative Subcell Absorber Layers: Bandgap Engineering*, Chowdhury Haque, **Philip (Sanghyun) Lee**,* University of Kentucky*; Kent Price,* Morehead State University

Tandem CdSeTe thin-film photovoltaic devices represent a promising frontier in solar energy technology, utilizing innovative bandgap engineering to enhance efficiency (>30 %) by broadening absorbing spectrum of impinging light. Although CdSeTe cells have been heralded for their high conversion efficiency (23.1 %), but limitations arise when single-junction designs fail to capture the full spectrum of solar radiation. Tandem devices (dual-junction or muti-junction) address this challenge by integrating multiple subcell absorber layers, each with optimized bandgap energy to selectively absorb different portions of the solar spectrum.

The introduction of alternative subcell absorber layers in the tandem structure is pivotal for expanding device performance by overcoming the fundamental limitation of a single-layer photovoltaic device by capturing larger ranges of wavelength of sunlight. Absorber layers are carefully selected and engineered to achieve bandgap tuning that maximizes spectral overlap while maintaining material compatibility. A top cell has larger bandgap, which can absorb shorter wavelength light. A bottom cell has smaller bandgap, capturing longer wavelength light.

For dual-junction tandem device configurations, we investigated the band alignment of top and bottom subcell materials to achieve the optimized bandgap between two subcells through bandgap engineering. From the theoretical study, bandgaps of dual-junction tandem devices are 1.5 - 1.8 eV and 1.4 - 1.5 eV for top and bottom (CdSeTe) subcells, respectively. The theoretical maximum power conversion efficiency (PCE) is 33.16 %. Multiple top and bottom absorber candidates were explored, including CdZnTe (Eg = 1.75-1.8 eV) and CdMnTe (1.7-1.75 eV) for a top subcell and CdSeTe (1.4 - 1.5 eV) for a bottom subcell. To optimize tandem devices, the current matching technique is used to determine the optimal thickness of each subcell. For the top layers, the thickness of CdMnTe is 450 nm, and for CdZnTe, it is 398 nm. The thickness of the bottom layer is approximately 2.4 um to achieve the best performance in a two-terminal tandem device. With spectral filtering and current matching, CdMnTe/CdSeTe tandem devices demonstrate an open-circuit voltage (Voc) of 1.52 V, a short-circuit current density (Jsc) of 15.7 mA/cm^2, and a fill factor (FF) of 82.1%, resulting in power conversion efficiency of 19.61 %. In contrast, CdZnTe/CdSeTe tandem devices demonstrate an Voc 1.51 V, Jsc 16.2 mA/cm^2, and FF 75.52 % with PCE 18.54 %. In summary, the best PCE is MgZnTe 19.61%, indicating that these devices are promising candidates for high-performance tandem solar cells.

EM-ThP-10 Ferroelectric Tunnel Junction NVM Stability*, **M. David Henry**,* Sandia National Laboratories

Ferroelectric $(Hf,Zr)O_2$-based tunnel junctions have shown significant promise as two-terminal resistive non-volatile memory (NVM) devices, exhibiting excellent area scaling capabilities and a high degree of compatibility with complementary metal-oxide-semiconductor (CMOS) technology. These devices can operate in a binary state, characterized by a high resistance state (HRS) and a low resistance state (LRS), as well as support multiple intermediate resistance states. From semiconductor physics, we describe the transport behavior using a combination of Ohmic conduction and Poole Frenkel (PF) defect mediated conduction. At low field (10^{-5}V/cm), Ohmic conduction dominates whereas at medium to high field a modified PF dominates. From the conduction mechanism, several factors can influence the stability of resistance states for a binary and multistate based devices including temperature, imprint, and even the act of reading out the state. This work will discuss these factors and demonstrate the functionality of these ferroelectric tunnel junction devices in both 5-bit and 4-bit configurations, enhancing data storage density and enabling advanced functionalities.

EM-ThP-11 Ab Initio Molecular Dynamics Modeling of Amorphous Titanium Silicon Nitride*, Somilkumar Rathi, Parag Banerjee,* University of Central Florida*;* ***Raymond Atta-Fynn,*** Los Alamos National Laboratory

Amorphous titanium silicon nitride is a ceramic material that has emerged as a strong candidate for a next-generation, ultra-thin diffusion barrier material in semiconductor device fabrication. As device dimensions shrink, TiSiN is increasingly considered a viable alternative to traditional TaN- and TiN-based barriers due to its structural tunability (crystalline to amorphous) enabled by doping. Moreover, its ease of synthesis and electrical properties are comparable to those of conventional barrier materials even at much lower thicknesses, facilitating integration into advanced device nodes. In this work, *ab initio* molecular dynamics simulations based on the quench-from-the-melt technique were employed to model amorphous titanium silicon nitride by systematically doping stoichiometric TiN with Si until clear signatures of amorphization emerged.

We observed that the onset of amorphization occurs when the fraction of Si in TiN reaches at least 25%. The distributions of various bond lengths and bond angles were analyzed to gain insight into the geometry of the structures. The angular-momentum–resolved electronic density of states was used to analyze the interactions between the Ti, N, and Si electron states. The amorphization process is explained by the reduction in ionicity and the increase in covalency induced by Si incorporation.

EM-ThP-12 Spectroscopic Characterization and Defect Identification in Wide Bandgap Semiconducting Materials*,* ***Praveena Manimunda,*** HORIBA

Wide bandgap semiconductors such as silicon carbide and Ga_2O_3, are used in power electronics, high power and high temperature devices. Achieving defect free, doped wide bandgap semiconductors are still a challenge. In this study spectroscopic characterization techniques such as photoluminescence, Raman and cathodoluminescence methods are utilized to identify microscopic defects in 3C-SiC, n-type 4H-SiC and shape engineered SnO_2 nanostructures grown on Ga_2O_3 nanowires. Semiconducting oxide nanostructures with a wide range of morphologies are emerging as a viable candidate for applications such as optical and mechanical resonators and solar cells. However, attaining effectively doped oxide nanowires with controllable conductivity is still a challenge. [1,2] Designing semiconducting oxide nanostructures requires extensive understanding of their morphology and demands efficient multimodal characterization methods. Multimodal spectroscopy is the concept of combining several different spectroscopies onto one platform, thereby expanding the range of analytical capabilities available on that single platform. Besides the obvious benefit of cost reduction, having multiple analytical spectroscopies offers the added benefit of sample colocalization so that multiple complementary measurements can be made at the same location of the sample. The benefit of colocalization is particularly important as feature sizes get smaller, from a few microns to nanometers in size. Using patterned silicon grid sample and embedded position-sensing technology, coordinates of region of interest transferred between different spectroscopic tools. Raman, Photoluminescence, cathodoluminescence and Time Resolved Photoluminescence (TRPL) techniques were used to characterize growth induced defects.

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EM-ThP-13 Flexible Perovskite Solar Cells with Reusable Stainless-Steel Foil Substrates*,* ***Pramod Baral,*** Verde Technologies Inc.

Flexible Perovskite Solar Cells with Reusable Stainless-Steel Foil Substrates

Pramod Baral[1], Vivek Babu[1], Francesca Brunetti[2]

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2. *CHOSE (Centre for Hybrid and Organic Solar Energy), Department of Electronic Engineering, University of Rome Tor Vergata, 00133, Italy*

Perovskite solar cells (PSCs) have achieved power-conversion efficiencies (PCEs) of 27% on rigid glass substrates, yet their flexible counterparts are more attractive for lightweight, portable and roll-to-roll manufacturing applications. Conventional polymer substrates such as PET and PEN, however, are limited by low thermal tolerance, modest barrier properties, and single-use constraints. Here, we demonstrate stainless-steel (SS) foil as a multifunctional application that simultaneously serves as a flexible substrate, conductive bottom electrode, and robust barrier layer, offering high thermal and mechanical stability as well as reusability across multiple fabrication cycles. Our device stack SS/NiO_x/MeO-4PACz/PEAI/FAPI/3MTPAI/C_{60}/BCP/Cu fabricated via scalable slot-coating of the perovskite absorber and high-vacuum evaporation of the electron transport layer (ETL) and top electrode layers, achieves PCEs approaching 10% under standard 1-sun illumination. Performance is currently constrained by optical absorption losses in the semi-transparent Cu electrode, which limit photocurrent generation. To address this, we are transitioning to low-temperature high-vacuum sputtered transparent conducting oxides such as indium tin oxide (ITO) and indium zinc oxide (IZO), which offer higher transparency and lower sheet resistance while remaining compatible with roll-to-roll processing. This approach highlights a realistic pathway toward scalable flexible perovskite solar cells (FPSCs) exceeding 20% efficiency, enabling cost-effective deployment in building-integrated photovoltaics, mobile systems, and off-grid power applications.

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.

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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).

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