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

8:00am **EM1+AP+CPS+MS+PS+QS+SM+TF-TuM-1 Optical Integration for Trapped-Ion Systems***, **Daniel Stick,*** Sandia National Laboratories **INVITED**

First demonstrated in 2006, surface ion traps provide a platform for storing 2D arrays of ions and have been widely adopted across the trapped-ion quantum computing community. To take advantage of the scalability enabled by these devices, on-chip waveguides have been developed over the last decade to replace traditional bulk-optics that can only illuminate a single line of ions. Here I will describe integrated photonics experiments that bring together multiple elements to control larger arrays of ions, as well as new approaches to addressing the I/O challenge of bringing the many optical signals across the ultra-high vacuum boundary. These advances are necessary for supporting the large number of ions needed for trapped-ion quantum computing, as well as for making deployable optical clocks.

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**, Jean-Philippe Soulié, Daniel Perez Lozano, Gilles Delie, Ankit Pokhrel, Benjamin Huet,* IMEC Belgium*; Margriet J. Van Bael,* KU Leuven and Imec, Belgium*; Daan Buseyne,* KU Leuven, Belgium*; Blake Hodges, Seifallah Ibrahim, Sabine O'Neal,* Imec USA*; Zsolt Tökei,* Imec Belgium*; Anna Herr, Quentin Herr,* Imec USA

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

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

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

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9:30am **EM1+AP+CPS+MS+PS+QS+SM+TF-TuM-7 Photon Down-Conversion of Yb-Doped CsPb(Cl1-xBrx)3 to Low-bandgap Metal Halide Perovskites***, **Yutong Ren,*** 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.

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 Implementation of a Truly 2D Model to Describe the Weak Antilocalization Behavior of Topological Insulators***, **Ryan Van Haren,** Aubrey Hanbicki, Adam Friedman,* Laboratory for Physical Sciences

Topological insulators continue to garner interest for potential and functionally-prototyped applications in next-gen electronic, spintronic, and quantum devices. In many of these applications, the topological surface states play a critical role. Transport through the surface states is often quantified by fitting to quantum corrections to the conductance that appear at low temperature. The model commonly used for these fittings is the Hikami-Larkin-Nagaoka (HLN) model, a quasi-2D model that does not account for the Dirac nature of the topological surface state. In the years following the discovery of topological insulators, theoretical work was performed that calculated the quantum corrections while taking into account the unique properties of the topologically protected surface states[1]. This Dirac fermion model provides powerful insight into the surface state transport by quantifying the Fermi velocity and the phase coherence length, among other parameters, but adoption of this model has been slow due to it being more complicated to utilize than the HLN model. In this work, I will present my method for implementing the Dirac fermion model in practice on weak antilocalization data from topological insulator thin films of $Bi_{0.85}Sb_{0.15}$ and previously published topological insulator thin films[2]. I will contrast the Dirac fermion model fits with the HLN model fits and show how the derived Fermi velocity agrees well with values derived from ARPES measurements reported in literature. I will make the argument that, while the HLN model still has its uses, analysis of weak antilocalization behavior in topological insulators is incomplete without utilization of the Dirac fermion model.

(1) Adroguer, P.; Liu, W. E.; Culcer, D.; Hankiewicz, E. M. Conductivity Corrections for Topological Insulators with Spin-Orbit Impurities: Hikami-Larkin-Nagaoka Formula Revisited. *Phys. Rev. B* **2015**, *92* (24), 241402. https://doi.org/10.1103/PhysRevB.92.241402.

(2) Van Haren, R.; Lederman, D. Suppressed Weak Antilocalization in Topological Insulator--Antiferromagnetic Insulator $(BiSb)_2Te_3$-MnF_2 Thin Film Bilayers. *Phys. Rev. B* **2024**, *110* (20), 205409. https://doi.org/10.1103/PhysRevB.110.205409.

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

Evolution of Materials and Devices for Energy Harvesting and Conversion

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

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

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

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

11:15am **EM2+AP+QS+TF-TuM-14 Analysis of KNbo$_3$ Crystal Structure Fabricated on LiNbO$_3$ and LiTaO$_3$ Substrate for Piezoelectric Sensors and Devices Applications***, **LAY THITHI,** Asuki Hagiwara, Ryotsuke Arai,* Josai University, Japan

Recently, small scales energy harvester with clean energy sources are in demand for various portable sensors and electronics devices [1]. Piezoelectric materials such as $KNbO_3$ are in focus for new type of sensors and electronic materials due to its high piezoelectric properties, high curie temperature around 450°C 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].

[1] 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.

[2] Ryo Kudo, Peter Bornnann, Tobias Hemsel and Takeshi Morita, Thick KNbO3 film deposited by ultrasonic-assisted hydrothermal method, acoust. Sci. & Tech. 36, 3262-264, 2015.

[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.

[5] Xiaoyan Liu, Kazuya Terabe and Kenji Kitamura, Stability of engineered domains in ferroelectric LiNbO3, LiTaO3, crystals, Phys. Scr. T129, 103-107, 2007.

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.

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

Moderators: Alain Diebold, University at Albany-SUNY, **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 Collaborative AI - Driving Innovation and Sustainability in Semiconductor Industry***,* ***Julien Baderot****, Ali Hallal, Hervé Ozdoba, Johann Foucher,* Pollen Metrology, France

In the rapidly evolving landscape of semiconductor technologies, the integration of artificial intelligence (AI) is fastening the way we approach material characterization, and process optimization. By leveraging computational power and collaborative AI technology, we can accelerate innovation, enhance efficiency, and promote sustainability across the industry.Collaborative AI facilitates the development ofmodels to automate analyses and the usage of IA between integrated circuitmanufacturers, equipment suppliers and internal software development.This approach addresses the growing challenges of process variability, rising complexity, and increasing quality demands, while also reducing environmental impact by boosting process yield.

Every device development requires process iteration with significant economical, human and environmental costs. As the industry seeks more effective means of advancing technology, collaborative AI emerges as a critical driver of performance and sustainability. Each user can accelerate theirowninnovation roadmap with faster data analytics at all levels.Ouron-premise platform guarantees full control over intellectual property while benefitingfrom a collective knowledge base from open-source data. Finally, by reducing the need for redundant tests and reaching specifications with fewer experiments, collaborative AI promotes a more environmental-friendly approach to innovation.

To answer the needs of the semiconductor industry, our collaborative platform embeds three key application modules. First, SmartMet3 defines precise recipes for material characterization and employs deep learning methods to replicate measurement strategies across multiple objects in images. It improves material characterization, enhances accuracy by reducing bias, and accelerates the transition from design to high-volume manufacturing. Then, SmartDef3 detects and measures defects using both supervised and unsupervised methods requiring low to no annotations. It incorporates clustering techniques to automatically identify new defect types, thereby improving defect detection and classification processes. Finally, SmartYield3 creates a digital twin of industrial processes, facilitating new experiments and defining optimal material targets. By reducing the number of physical experiments required to meet specifications, it enhances efficiency and accelerates the development cycle.

Our collaborative IA platform creates a common language between data, tools, and experts, transforming complexity into long-term value. Fewer tests, less wasted processes and more shared intelligence contribute to greater industrial sobriety and faster innovations.

4:45pm **EM2+AIML+AP+CPS+MS+SM-TuA-11 MOFCreatioNN: A Novel Modular Machine Learning Approach for Designing 'Undesignable' Metal-Organic Frameworks.***,* ***Satya Kokonda****,* 4779 Weatherhill Dr

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_2$62 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.

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

Thermal and Plasma-Enhanced Atomic Layer Deposition

Moderators: Adrie Mackus, Eindhoven University, Netherlands, **Austin Minnich**, California Institute of Technology

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

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

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

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

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

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

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

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

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

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

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

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

1. Kang et al. J. Nanosci & Nanotech. 19, 6232 (2019).
2. Conley, Jr. et al., Appl. Phys. Lett. 84, 1913 (2004).
3. Conley, Jr. et al., MRS Proc. Vol. 811, 5 (2004).
4. No *et al.*, J. ECS 153, F87 (2006).
5. Clark et al., ECS Trans. 41(2), 79 (2011).
6. Miikkulainen *et al.*, ECS Trans. 80(3), 49 (2017).
7. Holden *et al.* J. Vac. Sci. Tech. A. **40,** 040401 (2022).
8. Ueda *et al.*, Appl. Surf. Sci. 554, 149656 (2021).
9. Liu and Chang. J. Chem. Phys. 116, (2002).
10. Becher *et al.*, Adv. Eng. Mater. 2300677 (2023).
11. Kupp *et al.*, ALD 2024, Helsinki, AVS 2024 Tampa, submitted to JVSTA.

9:00am **AP+PS+TF-WeM-5 In Situ Studies of Ald Hf0.5Zr0.5O_2 by Spectroscopic Ellipsometry and Reflection Absorption Infrared Spectroscopy***, Stijn van der Heijden, Alex Neefs,* ***Erwin Kessels,*** *Bart Macco,* Eindhoven University of Technology, Netherlands

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

References

[1] Y. Deng, et al., International Interconnect Technology Conference (IITC), 3.2, San Jose, CA, June 2024.

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

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

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

References

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

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

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

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

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

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

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

Electronic Materials and Photonics
Room 207 A W - Session EM1+AP+CA+CPS+MS+TF-WeM
Advances in Wide Bandgap Materials and Devices

Moderators: Rachael Myers-Ward, U.S. Naval Research Laboratory, **Chris Richardson**, Laboratory for 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.

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

Thermal and Plasma enhanced Atomic Layer Etching

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Acknowledgement

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

[1] T.T.N. Nguyen *et al.*, Sci. Rep. **12**, 20394 (2022).

[2] B.S. Gottfried *et al.*, Int. J. Heat Mass Transf. **9**, 1167-1187 (1966).

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

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

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

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

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

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

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

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

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

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

Reference

1. *Proceedings of the International Conference on Advances and Applications in Plasma Physics (Aapp 2019)*, 2019.

2. *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films* **1989,** *7* (3), 686-690.

3. *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films* **1999,** *17* (6), 3179-3184.

4. *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films* **2021,** *39* (5).

4:15pm **AP+PS+TF-WeA-9 Damage-Free Atomic Layer Etching of SiO_2 Using Ultra-Low Electron Temperature Plasma***, **Junyoung Park**, Nayeon Kim, Jung-Eun Choi, Yujin Yeo, Min-Seok Kim, Chang-Min Lim, Beom-Jun Seo, Chin-Wook Chung,* Hanyang University, Korea

This work proposes an atomic layer etching (ALE) process utilizing ultra-low electron temperature (ULET) plasma, a damage-free plasma technique. The ULET plasma effectively suppresses charging and radiation damage due to its extremely low electron temperature, while its narrow ion energy distribution enables precise control of ion energy. These properties of ULET plasma facilitate faster CF polymer deposition during the surface modification step and induce sputtering at higher Vdc. After ULET plasma ALE, the surface roughness is approximately 3 nm, which is about one-fifth the level of that obtained with conventional plasma processes. In addition, the ALE process window is twice as wide as that of traditional methods, significantly improving process stability. These characteristics demonstrate that ULET plasma-based ALE is a promising technology for damage-free, atomic-scale etching required in next-generation semiconductor manufacturing.

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

References

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

5:30pm **AP+PS+TF-WeA-14 Atomic Layer Etching of Yttrium Orthovanadate Using Sequential Exposures of H_2 and SF_6/Ar Plasmas**, ***Mariya Ezzy****, Emanuel Green, Andrei Faraon, Austin Minnich,* California Institute of Technology

Yttrium orthovanadate (YVO4, YVO) is a promising host crystal for rare-earth ion (REI)-based quantum interfaces, such as ensemble-based quantum memories and single REIs in nanophotonic cavities, because of its high symmetry and high oscillator strength transitions. However, nanofabrication techniques for such complex oxide crystals are currently limited to physical etching techniques such as focused ion beam (FIB) milling. These physical etching techniques limit the quality factor (Q) of these nanophotonic resonator cavities, which are an order of magnitude less than their theoretical predictions, largely due to surface roughness scattering losses. Atomic layer etching (ALE) has the potential to mitigate this because of its ability to smooth surfaces down to the sub-nanometer scale. Here, we report the first ALE process for YVO using an H2 plasma modification step followed by an SF6/Ar plasma removal step. Preliminary results indicate an etch rate of 0.35 Å per cycle. The etch rates, surface morphology, and surface chemical composition are characterized using atomic force microscopy and x-ray photoelectron spectroscopy (XPS). The effect of ALE on the Q factor of FIB-milled nanophotonic cavities will also be discussed.

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

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

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

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

6:00pm **AP+PS+TF-WeA-16 Atomic Layer Etching for Vertical Trench Control and Electrical Optimization in HDLK Materials*****, Sanghyun Lee****, Keun Hee Bai,* Samsung Electronics, Republic of Korea

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

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, **Asif Kahn**, Georgia Institute of Technology

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

Hafnium oxide (HfO_2) shows significant potential for non-volatile memory and energy harvesting applications. However, its monoclinic phase lacks polarization, making it unsuitable for ferroelectric applications. Introducing ZrO_2 into HfO_2 (HZO) helps stabilize a ferroelectric phase. Atomic layer deposition (ALD) is the most widely used film processing technique, offering excellent thickness control, conformability, and relatively low processing temperature. Previous research has explored the impact of various metal precursors, oxidizer precursors, and process temperatures on the ferroelectric properties of HZO. One common observation is that the metal precursor purge time has a large effect on the resulting film phase and performance. However, no clear mechanism has been identified to explain this effect. In this presentation, we will discuss how HZO thin film properties change when the metal precursor purge time varies during plasma-enhanced ALD. Reducing the metal precursor purge time from 90 s to 3 s induced a transition from ferroelectric to antiferroelectric properties with double polarization hysteresis loops, higher endurance and polarization stability, and slightly increased in relatively permittivity.

Infrared spectroscopy measurements (FTIR-ATR) confirmed that the antiferroelectric properties are due to the antipolar orthorhombic o-I phase, which is consistent with observations from HRTEM and DPC-STEM. The films deposited with shorter purge times showed carbon impurities as identified by ToF-SIMS analysis. This suggests that residual chemical ligands from incomplete precursor removal during the ALD process, in part, stabilizes the antipolar o-I phase. These results show that phase stability in fluorite oxides is influenced by impurities beyond intentional substituents and that stable antiferroelectric responses can be achieved without deliberately altering the material composition, such as adjusting the Hf:Zr ratio to control phase formation.

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

Significant research has gone into understanding the stabilizing mechanisms and properties of ferroelectric hafnia. This is largely due to its ability to display ferroelectricity in size scales below 10 nm, incorporation in already existing mass production infrastructure, and complementary metal oxide semiconductor compatibility. Today, hafnium zirconium oxide (HZO) is the most studied hafnia alloy due to its low processing temperature. However, the widespread implementation of HZO as a memory material is hindered by a variety of challenges, such as wake–up, imprint, and retention. A major issue is the inability to make phase pure ferroelectric HZO, a metastable non–centrosymmetric polar orthorhombic structure. Commonly cited impurity phases include the metastable tetragonal, antipolar orthorhombic, and equilibrium monoclinic phases. Previous work using the atomic layer annealing (ALA) technique has shown enhanced crystallinity and remanent polarization in pristine HZO films, circumventing significant formation of the antiferroelectric and tetragonal phases. In this work, thin films of HZO were grown using the ALA technique with various ALA treatment durations, ranging from 0 s up to 59 s. Following a deposition of a metal oxide layer using plasma–enhanced atomic layer deposition, the surface of the film was subjected to additional argon plasma. After synthesis and a post–metallization anneal to form the metastable phase, various structural and electrical measurement techniques were used to characterize the films. Grazing-incidence X-ray diffraction shows no formation of the equilibrium monoclinic phase; Fourier transform infrared spectroscopy shows increasing ferroelectric phase concentration with ALA time. Polarization hysteresis measurements show an increasing hysteretic response with ALA time as compared to an antiferroelectric reference sample. Positive up negative down measurements quantified the relative amount of wake–up. The reference devices displayed a 200% increase in remanent polarization while the ALA samples displayed an 8% relative increase with the longest treatment time. The results suggest that ALA can modify the local environment of the deposited films, such that the phase fraction of the ferroelectric phase and the amount of wake–up can be tuned. This results in devices that exhibit minimal to no wake–up. This work furthers the understanding of the effect that ALA has on the resultant film's properties.

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

While research into understanding the performance-materials property relationship of hafnium zirconium oxide (HZO) based devices has been accelerated in the past decade, their integration into microelectronic products is challenged by their endurance and imprint behavior. Imprint, or a shift in the coercive field following polarization with an initial applied field, lowers HZO remanent polarization (P_r) along the imprint direction, impacting the current transport mechanisms and reducing the overall performance stability when studied in ferroelectric non-volatile memory applications. In these devices, imprint has been hypothesized to result from charge carrier migration at the electrode interface, increasing the charge needed for polarization switching. However, the mechanisms responsible for imprint in ferroelectric tunnel junctions (FTJ) is not understood. To study FTJ imprint phenomena, 7 nm $Hf_{0.7}Zr_{0.3}O_2$ devices with NbN and Nb as the top and bottom electrode, respectively, were fabricated. Polarization-electric field measurements were performed every 2^n seconds, showing a $+V_c$ shift with time. Resistance measurements, using a pulsing scheme composed of a $\pm V_{max}$ write pulse followed by fifty 0.4 V read pulses at various pulse widths taken every 2^n seconds, showed a drift in the ratio of high and low resistance states, and an overall reduction in the binary state memory window with increasing time, characteristic of imprint. Further, these results highlight imprint impacts on multi-state polarization switching used in neuromorphic memory applications. To investigate imprint mechanisms, pulsed hysteresis measurements taken in 0.1 V intervals followed by a reset pulse at $\pm V_{max}$ showed an 18.1x change in the resistance ratio between the high and low resistance states. However, a similar pulsed hysteresis measurement without the reset pulse had a 11.4x resistance ratio. These results support the generation of time-dependent imprint-free HZO-based FTJs by utilizing selective pulsing schemes, promoting their use in next-generation microelectronics.

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

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

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

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

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

Advances in Materials and Devices for Energy Storage

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

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

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

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

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

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

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

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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

Moderators: Heeyeop Chae, Sungkyunkwan University (SKKU), **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,*** 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*, 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.

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**,* 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.

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.

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

Emerging Applications for Atomic Scale Processing (ALD/ALE) including Precursors and Surface Reactions

Moderators: Robert Bruce, IBM Research, T. J. Watson Research Center, **John F. Conley, Jr.**, Oregon State University

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

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

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

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

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

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

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

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

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

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

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

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

Acknowledgements: This work was supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, Materials Science and Engineering Division.

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

The Semiconductor industry is struggling to continue to follow Moore's Law. For both technical and economic reasons, it is likely that the ASML High-NA Extreme Ultraviolet Lithography (EUV) tools will be the last photolithography technology to push to higher resolutions. Simultaneously, E-Beam Lithography (EBL) mask writers, while improving throughput by going highly parallel, are also very near the end of resolution improvements. The industry does not appear to expect any significant downscaling of devices beyond what will be possible with the ASML High-NA EUV tool which has a resolution of 8 nm.

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

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

3:45pm **AP+PS+TF-ThA-7 Chemistry of a 2D Material Fe_3GaTe_2 for Atomically-Precise Processing: Etching and ALD***, **Marissa D. Piña**, Andrew V. Teplyakov,* University of Delaware

Fe_3GaTe_2 is a 2D van der Waals material that displays intrinsic ferromagnetism above room temperature along with strong perpendicular anisotropy, making it a possible candidate for spintronics and magnonics applications. Recent computational studies have shown that the Fe_3GaTe_2 Curie temperature becomes elevated and its magnetic properties are tunable at the monolayer, demonstrating the importance of obtaining ordered and defect-free thin film and monolayer structures of this material by using atomically-precise treatments.

To determine whether Fe_3GaTe_2 can be etched controllably in nearly atomic layer etching regime, we performed a chlorine gas dose followed by an acetylacetone dose on Fe_3GaTe_2 flakes exfoliated onto a silicon substrate. AFM and XPS after the chlorine dose at elevated temperature show a partially etched but rougher surface. The consequent acetylacetone dose at the same temperature shows further etching. We aim at exploring atomic layer etching of Fe_3GaTe_2 under further optimized and controlled conditions. We are also exploring the etching mechanism to determine why the chlorine dose causes the initial change.

To explore the role of surface structure and chemistry of Fe_3GaTe_2 in ALD reactivity and also to determine whether ALD is feasible on Fe_3GaTe_2 flakes, we followed the ALD of Al_2O_3 on unmodified Fe_3GaTe_2 flakes. We observed alumina growth from TMA/water deposition cycles on Fe_3GaTe_2 after 10 and 30 cycles in a similar amount compared to what was grown on the reactive silicon substrate, as confirmed by ToF-SIMS depth profiling. We are currently evaluating the changes in Al_2O_3 growth after chemical surface modification of Fe_3GaTe_2 with small organic molecules.

4:00pm **AP+PS+TF-ThA-8 Optimizing Semiconductor Wafer Manufacturing with Proper Thermal Management***, **Margaret Brennan**,* Swagelok Company

This presentation by Margaret Brennan, Applications Solution Principal Engineering Lead, addresses the critical role of thermal management in semiconductor wafer manufacturing, with a specific focus on the thermal loop system. The thermal loop provides essential cooling to semiconductor wafers and requires precise temperature control to maintain optimal manufacturing conditions. The presentation highlights three key reasons for properly insulating the thermal loop: improving chiller efficiency, maintaining thermal stability for higher yields, and preserving uptime by preventing condensation issues.

Various insulation options are compared, ranging from basic covered hoses to high-performance vacuum jacketed solutions, with each offering different temperature ranges and performance characteristics. The presentation emphasizes that proper installation is equally important as product selection, with considerations for spacing, bending, air flow, and environmental conditions all affecting performance. As semiconductor manufacturing trends toward increasingly lower temperatures (projected to reach -120°C by 2027), advanced insulation technologies like vacuum barriers are becoming essential to eliminate convection heat transfer.

The presentation concludes by emphasizing the value of effective thermal management solutions that can reduce downtime, increase yields, and improve overall efficiency in semiconductor manufacturing operations.

About the speaker:

Margaret Brennan began her career as a mechanical design engineer responsible for developing blueprints for various construction projects across the higher education, healthcare, and medical research industries. She joined Swagelok Company in 2023 as a semiconductor application solutions engineer, where she supports the Swagelok sales and service network by developing solutions to address customer needs the semiconductor market.

Swagelok is a worldwide leader in industrial fluid systems—founded in 1947 on the merits of its revolutionary, leak-tight tube fitting. Swagelok has been servicing the semiconductor industry since the 1950s and provides fluid system products, assemblies, services, and training worldwide. With over 50 years of semiconductor innovation, the company introduced VCR fitting technology in 1968, expanded high-purity manufacturing capacity, continues to grow its workforce to adapt to business cycles, and employs knowledgeable specialists globally to support customer needs. Discover more at swagelok.com [http://www.swagelok.com/]

Atomic Scale Processing Mini-Symposium
Room Ballroom BC - Session AP-ThP
Atomic Scale Processing Poster Session

AP-ThP-2 Thermal Atomic Layer Etching of Lanthanum Oxide Using Acetylacetone and Ozone*, **Aziz Abdulagatov**, Jonathan Partridge,* University of Colorado at Boulder*; Charles Dezelah,* ASM Microchemistry Ltd., Finland*; Steven George,* University of Colorado at Boulder

Thermal atomic layer etching (ALE) of lanthanum oxide (La_2O_3) was demonstrated using sequential exposures of acetylacetone (Hacac) and ozone (O_3). Hacac reacts with La_2O_3 by a ligand addition and hydrogen transfer reaction to form volatile $La(acac)_3$ and H_2O according to: La_2O_3 + 6Hacac → $2La(acac)_3$ + $3H_2O$. Ozone was then used to remove carbon residue resulting from Hacac exposure on the surface.

In situ spectroscopic ellipsometry (SE) was used to monitor the film thickness change with number of ALE cycles. SE observed the linear decrease of La_2O_3 film thicknesses versus number of Hacac and O_3 cycles. Semicrystalline La_2O_3 thin films displayed etch rates of 0.2, 0.4 and 0.69 Å/cycle at 230, 250 and 270 °C, respectively. The SE studies also showed that the Hacac and O_3 surface reactions were self-limiting.

Atomic force microscopy (AFM) analysis of semicrystalline La_2O_3 on Si with a thickness of 20 nm displayed surface smoothing versus ALE cycles.The RMS surface roughness was 3.3 Å prior to ALE and 0.9 Å after ALE. Quadrupole mass spectrometry (QMS) was also utilized to study the Hacac-O_3 etch process on crystalline La_2O_3 powder at 250 °C. $La(acac)_3$ organic fragments were detected during Hacac exposure.During O_3 exposure, combustion products were observed from the oxidation of organic residuals left from Hacac exposures.

Hexafluoroacetylacetone (hfacH) has also been utilized instead of Hacac to etch La_2O_3. One advantage of Hhfac over Hacac is that Hhfac has a lower pKa value and hfac-metal complexes are generally more volatile. However, La_2O_3 ALE using hfacH and O_3 displayed a substantially lower etch rate of 0.06 Å/cycle at 250 °C.This result was attributed to significant film fluorination by Hhfac as revealed by XPS analysis. Etching lanthanum fluoride using the Hhfac-O_3 chemistry is more challenging.

AP-ThP-3 Spontaneous Etching of SiO2 by Co-Adsorbing Polar Molecules with HF*, **Marcel Junige**, Steven M. George,* University of Colorado Boulder

Spontaneous etching is characterized by a physicochemical reaction of a thin film surface with a reactant vapor that releases volatile products with a continuous etch rate. Spontaneous etching provides the benefit of a single processing step with simply one etchant exposure, as well as typically high inherent selectivity.

Previous work has demonstrated that anhydrous HF vapor does not spontaneously etch SiO_2. However, co-adsorbing ammonia (NH_3) with HF has led to rapid SiO_2 spontaneous etching. These results have suggested that the nature of the active etch species changes in the presence of NH_3. Without co-adsorbed NH_3, the active etch species is believed to be F^-. With the polar NH_3 co-adsorbate, the active etch species is thought to switch to HF_2^-. [Junige, George: *Chem. Mater.* **36**, 6950 (2024)]

Co-adsorbing polar molecules with HF has been proposed to form HF_2^- species to enable SiO_2 etching. Examples of suitable polar molecules include dimethylamine ($(CH_3)_2NH$: 1.0 D), NH_3 (1.4 D), methanol (CH_3OH: 1.7 D), water (H_2O: 1.85 D), or ethylene glycol ($(CH_2OH)_2$: 2.28 D); where the number in parentheses refers to the dipole moment of the respective molecule in the gas phase. In theory, these polar co-adsorbates solvate HF and stabilize the dissociation products H^+ and F^-. As a result of this more extensive HF dissociation, F^- species at increased concentration react further with HF to produce HF_2^- species.

In situ spectroscopic ellipsometry (iSE) experiments were performed to test the idea that other polar molecules co-adsorbed with HF may enable SiO_2 spontaneous etching. These investigations revealed that co-adsorbing H_2O or CH_3OH with HF did not spontaneously etch SiO_2 at 200 or 275°C. The adsorption and desorption kinetics of H_2O or CH_3OH molecules at SiO_2 surfaces might not yield an adequate solvation layer at these elevated temperatures. In contrast, co-adsorbing DMA+HF enabled SiO_2 spontaneous etching with a substantial etch rate of 34.70 Å/min at 200°C. Similar results have been observed previously for NH_3+HF co-dosing at 275°C. These results suggested that co-adsorbing polar molecules with HF to form HF_2^- species can etch SiO_2 if there is sufficient solvation. Co-adsorbing $(CH_2OH)_2$+HF, as well as $(CH_2OH)_2$ adsorbed layers on SiO_2 surfaces, may be tested in future experiments.

AP-ThP-4 Selective growth of WSe_2 through bioinspired seeding and vapor-based microreactor assisted nanoparticle deposition*, **Kylee Lamberson**, Chih-hung Chang,* Oregon State University

Microelectronic and photovoltaic technologies rely on safe, scalable, bottom-up fabrication strategies for high-performance semiconducting materials. Tungsten selenide (WSe_2), a transition metal dichalcogenide with a relatively large band gap, is particularly promising for micro- and optoelectronic applications. In this work, we introduce a bio-inspired approach and our patented vapor-based microreactor assisted nanoparticle deposition (V-MAND) to achieve area-selective atomic layer deposition (AS-ALD) of WSe_2. Our selectivity strategy draws inspiration from the ovipositor mechanism of the parasitic wasp *Diachasmimorpha longicaudata*. This species detects a host's location by their kairomones before depositing eggs. Similarly, we developed a seeding method using silica (SiO_2) nanoparticles to mimic alcohol (OH)-containing kairomones, promoting localized nucleation of WSe_2. Uniform, high-density OH coverage on the SiO_2 was achieved via piranha treatment, enhancing chemical affinity with tungsten precursors. To perform AS-ALD on the seeded regions with tunable thickness, vaporized tungsten carbonyl ($W(CO)_6$) and in situ generated hydrogen selenide (H_2Se) were delivered using the V-MAND system in between alternating flows of inert gas. H2Se was safely produced on-demand by reacting solid selenium powder with forming gas, avoiding the need for bulk storage of this hazardous precursor. Growth behavior was investigated by adjusting precursor delivery rates. Film composition and structure were characterized using SEM, AFM, FTIR, and XPS. This study demonstrates a novel and safe strategy for AS-ALD of WSe_2 and showcases the potential of V-MAND for scalable fabrication of 2D semiconductors.

AP-ThP-5 Selective Ruthenium Capping on Copper over SiO_2: A Combined DFT and In Situ QCM Study*, **Yoonho Choi**, Mi-Soo Kim, Okhyeon Kim, Tanzia Chowdhury, Khabib Khumaini, Hye-Lee Kim, Won-Jun Lee,* Sejong University, Republic of Korea

Metal capping plays a crucial role in enhancing the reliability of copper (Cu) interconnects. It has been also studied for low-temperature hybrid bonding of Cu pads. Recent studies have explored the selective deposition of ruthenium (Ru) as a capping material,[1] but the underlying mechanism of this selective deposition remains unclear. In this study, we investigate the mechanism of selective Ru deposition on Cu surfaces in contrast to SiO_2 by employing both density functional theory (DFT) calculations and in situ quartz crystal microbalance (QCM) analysis. DFT calculations simulate the chemisorption of the Ru precursor, (Me-CHD)$Ru(CO)_3$, on various substrates, including Cu, OH-terminated SiO_2, and CH_3-terminated SiO_2. We compare the reaction and activation energies for chemisorption with and without the addition of H_2. Additionally, in situ QCM analysis allows us to monitor the growth behaviors on different surfaces simultaneously, enabling the determination of incubation periods and the maximum thickness of selective capping. The DFT simulations align closely with experimental observations, confirming the selective growth mechanism of Ru on Cu surfaces. Our findings provide critical insights into the selective deposition process, offering a deeper understanding of Ru capping for advanced interconnects.

References

1. Mandal A.K., van der Veen M.H., Haghighi N.R, Robin M., Claessens N., Meersschaut J., Jourdan N., Tokei Z., Delabie A., *Adv. Mater. Technol.* **2024**, 9, 2301820.

AP-ThP-6 Atomic Scale Processing (AP7) Sustainable Semiconductor Manufacturing (SM): Oral Session (or Poster)DOE's Sandia Project on Tunnel Field Effect Transistor (TFET) for 10X Microelectronics Energy Efficiency in a General Purpose Transistor. Desiree Salazar, E. Lozier, S. Misra6 and T. Kaarsberg1*, **Desiree Salazar**,* CLEAResult Energetics, DOE/AMMTO*; Emilie Lozier,* DOE-EERE*; Shashank Misra,* Sandia National Lab*; Tina Kaarsberg,* DOE-EERE

Abstract—The United States Department of Energy (DOE) Advanced Materials and Manufacturing Technology Office (AMMTO) is leading a multi-organization effort to counter alarming trends in U.S. computing energy use (e.g. **LBNL 2024 forecasts -** lbnl-2024-united-states-data-center-energy-usage-report.pdf [https://eta-publications.lbl.gov/sites/default/files/2024-12/lbnl-2024-united-states-data-center-energy-usage-report.pdf] - that data centers will account for 26% of US electricity use by 2028 when cyrptomining is included) with its initiative in energy efficiency scaling for two decades (EES2) for microelectronics.Under this initiative, DOE/AMMTO has funded a portfolio of EES2 device technology R&D projects that promise >10X energy efficiency increase by 2030. This [talk] will highlight the first of these projects with Sandia National Laboratories to build on atomically precise manufacturing techniques to create a vertical tunnel field effect transistor (vTFET). Updates will be provided on the successful integration of front end of line (FEOL), back end of line (BEOL) and mid-end of line (MEOL) manufacturing processes (especially thermal budget) to fabricate this vTFET in a CMOS compatible process.One important discovery of the research in this area is “ultradoping” which makes the abrupt doping profiles needed for efficientvTFETs far more manufacturable. This talk also will present how these Sandia results integrate with version 1.0b of the EES2 roadmap that will be issued in Summer 2025. Version 1.0a of the Roadmap is available at EES2 Roadmap Version 1.0 [https://eere-exchange.energy.gov/FileContent.aspx?FileID=f4234e29-cc0c-4a56-a510-86b616ab5535] .

AP-ThP-7 Atomic Layer Deposition of Vanadium Oxide on Silicon Oxide and Kapton Substrates*, **Mohamed Asrif**,* North Carolina A&T State University

Multilayer optical coatings play a vital role in the propagation of light in photonic devices through selective reflection, transmission, and absorption of specific wavelengths. Among transition metal oxides, Vanadium Oxide (VO2) shows significant promise due to its high corrosion resistance at low temperatures, high tensile strength, and high electrical conductivity. This work aims to enhance the performance and durability of optical coatings by depositing VO_2 thin films using Atomic Layer Deposition (ALD), a technique offering precise and conformal deposition of ultra-thin films with Angstrom-level thickness control at low temperatures, making it a preferred method of growing thin films on planar and nanostructured surfaces. Vanadium Oxide (VO2) films were synthesized on Silicon and Kapton Substrates by the ALD method using the precursor Tetrakis (ethylamino) vanadium (TEMAV). Results from XPS confirmed successful deposition, as the binding energies for vanadium (V2p ½ and V2p 3/2 orbitals were both present) and oxygen were both present, as well as residual traces of Carbon and Nitrogen. XRD measurements for the 7 nm sample and the 21 nm sample revealed that the films were amorphous, deposited at 150 °C. AFM results indicated mostly smooth surfaces with an RMS roughness value of between 0.2 and 0.3 nm. However, on a larger scale, that RMS roughness value increased to around 17 nm, indicating that there were signs of agglomeration in the deposition. Raman spectroscopy of the 21 nm sample exhibited spectral features corresponding to mixed oxidation states of vanadium, suggesting partial crystallinity post-annealing. Characterization of the 42 nm samples are still in progress. Post-deposition annealing at ~500 °C in ultra-high vacuum will be utilized to generate crystallization, then samples will undergo comprehensive determination of the structural and surface chemistry.

AP-ThP-8 Development of ALD-ZrN for Diffusion Barrier Layer in ULSI-Cu Interconnects*, Jun Tanaka, Jun Yamaguchi, Noboru Sato, Naoki Tamaoki, Atsuhiro Tsukune, **Yukihiro Shimogaki**,* The University of Tokyo, Japan

To achieve higher performance and lower power consumption in ULSI devices, transistors have been continuously miniaturized and integrated at higher densities, resulting in the reduction of Cu interconnect linewidths. However, as the linewidth approaches the mean free path of electrons in Cu (~40 nm), the effects of inelastic electron scattering at grain boundaries and sidewall interfaces become non-negligible, leading to increased resistivity. Furthermore, the conventional diffusion barrier TaN, used to prevent Cu penetration into interlayer dielectrics, has a much higher resistivity than Cu (Cu:1.68 μΩ·cm, TaN:135 μΩ·cm), and its thickness reduction is limited due to the need to maintain barrier integrity. As a result, the proportion of Cu in the interconnect cross-section decreases with scaling, causing a sharp increase in line resistance. Additionally, increased resistance at the via bottom due to the barrier layer also becomes problematic.

In this study, we focused on ZrN as a novel diffusion barrier material. ZrN possesses the lowest resistivity (13.6 μΩ·cm) among transition metal nitrides [1] and maintains its barrier properties even after annealing at 500 °C [2]. To deposit ZrN films, we employed thermal atomic layer deposition (ALD), which is suitable for conformal coating in narrow damascene trenches. $Zr[N(CH_3)_2]_4$ was used as the precursor, NH_3 as the reactant gas, and N_2 as the carrier/purge gas.

Figure 1 shows the thickness and resistivity of ZrN films deposited at 250 °C as a function of ALD cycles. Film thickness increased linearly with the number of cycles, indicating excellent controllability, although the resulting resistivity was not yet ideal. Figure 2 presents the growth per cycle (GPC) at various deposition temperatures, revealing a stable ALD window between 150 and 250 °C. Figure 3(a) shows the dependence of film density and resistivity on NH_3 supply time for ZrN deposited at 200 °C, which lies within the ALD window. Increasing the NH_3 supply time led to higher film density and lower resistivity. Since no significant change in film composition was observed by XPS (Fig. 3(b)), the densification is attributed to improved surface reactions during the NH_3 pulse. When a film deposited with a 5 sec NH_3 supply was etched using an Ar ion gun in the XPS chamber and its resistance measured, removal of the surface oxide layer significantly reduced the resistance (Fig. 4). Suppressing surface oxidation at elevated temperatures after deposition is expected to further reduce the resistivity.

[1] C. C. Wang *et al*., *Journal of Materials Science*, **30**, 1627–1641 (1995).

[2] M.B. Takeyama *et a*l., *Japanese Journal of Applied Physics*, **61** SJ0802 (2022).

AP-ThP-9 Comparative Evaluation of SiO2 Atomic Layer Etching Using NF3 and SF6 Gases via a Combined Thermal and Remote Plasma Approach*, **Min Kyun Sohn**, Jieun Kim, Sun Kyu Jung, Min-A Park, Jin Ha Kim, Jaeseoung Park, Subin Heo, Sang-Hoon Kim, Jeong Woo Park, Seong Hyun Lee, Dongwoo Suh,* Electronics and Telecommunications Research Institute, Republic of Korea

Atomic Layer Etching (ALE) is a critical technology enabling atomic-scale precision in advanced semiconductor device fabrication. Although obtaining detailed etching characteristics from various fluorine-based gases is crucial for optimizing etch per cycle (EPC) and selectivity, experimental data on gases other than commonly used hydrogen fluoride (HF) or C-F combined gases remain limited. This study investigates silicon dioxide (SiO_2) ALE processes utilizing sulfur hexafluoride (SF_6) and nitrogen trifluoride (NF_3) gases, employing a combined thermal and remote plasma-assisted approach at a process temperature of 300°C. The selection of SF_6 and NF_3 gases was guided by their distinct environmental impacts, radical generation efficiencies, and their potential effects on etching characteristics.

In this study, a surface modification approach using trimethylaluminum (TMA), followed by selective removal with remotely generated fluorine radicals, was systematically evaluated. By combining thermal isotropic surface modification with highly reactive fluorine radicals generated via remote plasma, this method effectively leverages the advantages of both isotropic thermal etching and plasma-enhanced high EPC. Experimental results indicated that NF_3 gas generated significantly higher fluorine radical densities than SF_6 under identical thermal and remote plasma conditions, resulting in enhanced EPC. However, in the case of NF_3 gas flow rates above 20 sccm, the significantly higher density of fluorine radicals generated expanded beyond the ALE regime into conventional plasma etching territory, limiting uniform atomic-level control. In contrast, fluorine radicals generated by SF_6 remained within optimal quantities for true ALE conditions, even at a relatively high flow rate of 100 sccm. Additionally, the remote plasma-assisted method effectively minimized ion-induced surface damage, thus promoting superior etching quality.

Our findings highlight that selecting the appropriate gas (NF_3 or SF_6) based on specific process requirements is critical, as each gas offers distinct advantages. Future research will explore mixed-gas processes combining SF_6 and NF_3 to synergistically enhance their respective benefits and further optimize ALE performance.

AcknowledgmentsThis work was supported by the Electronics and Telecommunications Research Institute(ETRI) grant funded by the Korean government [25ZH1240]

AP-ThP-10 High-rate Isotropic Atomic Layer Etching of HfO_2 with Fluorine Radicals and Metal Precursor*, **Jehwan Hong**, Gyejun Cho, Hye-Lee Kim,* Sejong University, Republic of Korea*; Byungchul Cho,* Wonik IPS, Republic of Korea*; Won-Jun Lee,* Sejong University, Republic of Korea

Hafnium oxide (HfO_2) thin films are widely used as high-k dielectrics in semiconductor devices due to their high dielectric constant and low leakage current. These films are mainly deposited by atomic layer deposition (ALD), which is generally known to produce films with ultra-smooth surfaces. However, the surface roughness of ALD-deposited films tends to increase with decreasing film thickness, which negatively affects device performance. To overcome this problem, a strategy has been proposed in which thicker ALD HfO_2 films are first deposited and then thinned by atomic layer etching (ALE) to obtain smoother ultrathin films [1]. Conventional thermal ALE using hydrogen fluoride (HF) allows atomic-scale etch control but suffers from slow reaction kinetics due to the low reactivity of HF, which limits process throughput. In particular, crystalline HfO_2 films exhibit significantly lower etch rates than amorphous HfO_2 films. In this study, ALE was performed by alternating exposure to fluorine (F) radicals and metal precursors. The self-limiting etch behavior was verified by in situ quartz crystal microbalance (QCM) measurements, and the etch rates were studied as a function of process temperature. The changes in the HfO_2surface during the ALE process under different conditions were characterized to elucidate the etching mechanism. The F-radical-based ALE process developed in this study exhibits a higher etch rate than the HF-based ALE process. In particular, crystalline films show an etch rate similar to that of amorphous films, which is in contrast to the HF-based process. The effects of ALE on surface roughness and electrical properties were also analyzed, and the underlying causes of these changes were discussed.

References [1] S.M. George et al., ACS Nano 10 (2016) 4889–4894.

AP-ThP-11 Characterizing Remote Ar/H2 plasmas for Atomic Precision Processing*, **David Boris**, Maria Sales, Peter Litwin, Michael Johnson, Mackenzie Meyer, Virginia Wheeler, Jeffrey Woodward, Scott Walton,* U.S. Naval Research Laboratory

In comparison to thermal atomic layer deposition (ALD) plasma-enhanced atomic layer deposition (PE-ALD) generally offers the benefit of substantially reduced growth temperatures and greater flexibility in tailoring process conditions to achieve desirable film characteristics. Among the approaches used to tailor film properties is the inclusion of Ar/H2 plasma exposures in the PEALD growth cycle as a means to either mitigate carbon contamination or as a reduction step that converts metal oxide films to metallic films. When employing these Ar/H2 plasma exposures however, control over the flux and energy of ions is needed to avoid unwanted damage to the growth surface. In addition, Ar/H2 plasmas produce atomic H radicals, and VUV photons which also need to be considered when choosing process conditions. In this work we aim to characterize the production of ions, atomic neutrals, and photons within remote Ar/H2 inductively coupled plasma sources commonly used for PEALD. The information gained in characterizing these systems will then be used to guide the choice of process conditions for PEALD growths involving Ar/H2 plasma exposures. Langmuir probe and retarding field energy analyzer (RFEA) measurements were used to characterize the charged particle flux within these systems, and optical emission and VUV emission spectroscopy was used to characterize the atomic H density and VUV photon characteristics respectively. This work is supported by the Office of Naval Research through the Naval Research Laboratory base program.

AP-ThP-12 From Inhibitor to Promoter: Role of Hexafluoroacetylacetone in Tailoring TiO_2 Growth on MgO Surfaces*, **Sanuthmi Dunuwila**, John R. Mason, Andrew Teplyakov,* University of Delaware

Magnesium oxide (MgO) is a key material in electronic and optoelectronic devices due to its wide bandgap, optical transparency, and thermal stability. However, the performance of MgO-based multilayer systems is often limited by interfacial inconsistencies, especially when deposited via such techniques as sputtering, which introduce surface defects. Surface modification strategies have emerged to address these issues, particularly in enhancing compatibility with atomic layer deposition (ALD) processes.

This work explores the surface modification of sputter-deposited amorphous MgO films using 1,1,1,5,5,5-hexafluoro-2,4-pentanedione (hfacH), a fluorinated β-diketone. Although this compound has been reported as a small-molecule inhibitor in selected ALD processes, this study demonstrates that hfacH acts as a growth promoter for TiO_2 deposition on MgO with thermal ALD that utilizes TDMAT and H_2O as co-reactants. Water contact angle (WCA) measurements confirm that hfacH alters the MgO surface from hydrophilic to hydrophobic, yet TiO_2 nucleation is enhanced on the modified surface, challenging conventional interpretations of surface energy and precursor accessibility.

This study uses a suite of primary surface characterization tools, X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), time-of-flight secondary ion mass spectrometry (ToF-SIMS), X-ray diffraction (XRD), and scanning electron microscopy (SEM) to confirm successful TiO_2 deposition.

These findings challenge the prevailing notion of hfacH as a growth inhibitor and highlight its context-dependent behavior. The modified surface facilitates nucleation, likely due to altered surface energy and local chemical environment, suggesting a potential role for hfacH as a growth promoter. This study contributes to the understanding of molecular surface chemistry and offers new insight into improving interface quality in multilayer oxide systems.

By redefining the function of fluorinated ligands in ALD chemistry, this work opens opportunities for more controlled and efficient deposition strategies in advanced electronic device fabrication.

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

9:00am **AP+EM+PS+TF-FrM-4 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).

9:15am **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 Towards Area Selective Deposition: Photoassisted Chemical Vapor Deposition Using Ru Precursors***, **Christopher Brewer**,* University of Texas at Dallas*; Rashmi Singh, Bishwaprava Das,* University of Florida*; Diego Caretti, Dyotana Bhattacharyya, Oluwatamilore Oni,* University of Texas at Dallas*; Xin Kang, Jonah Perry, Lisa McElwee-White,* University of Florida*; Amy Walker,* University of Texas at Dallas

Photoassisted chemical vapor deposition (PACVD) is an attractive technique for the metallization of thermally sensitive films, such as organic thin films.A library of (η^4-diene)Ru(CO)$_3$ and (η^2-olefin)Ru(CO)$_4$ precursors has been developed that demonstrate photolytic loss of both CO and alkene ligands at room temperature.Using $-CH_3$, -OH, and -COOH terminated self-assembled monolayers (SAMs) as model substrates, we have investigated the use of these precursors in area selective deposition. We demonstrate that the (η^4-diene)$Ru(CO)_3$ precursors show a strong deposition preference onto -COOH functionalized SAMs, while (η^2-olefin)$Ru(CO)_4$ precursors show a deposition preference onto the -COOH and -OH functionalized SAMs.The $-CH_3$ functionalized SAMs are a non-growth surface for all the precursors screened.Using X-ray photoelectron spectroscopy, we have elucidated the composition of the deposited Ru species. Using these results we shall discuss new potentially effective PACVD precursors for the deposition of other metals.

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).

11:30am **AP+EM+PS+TF-FrM-14 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).

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