Tutorial

Room Ybor Salons I-IV - Session TS-SuA

Tutorial Session

Moderators: Parag Banerjee, University of Central Florida, **Nathan Marchak**, IBM, **Christophe Vallée**, University of Albany, **Virginia Wheeler**, U.S. Naval Research Laboratory

1:00pm **TS-SuA-1 Connection between Precursor Molecules and ALD/ASD/ALE Processes**, ***Atsushi Sakurai***, ADEKA CORPORATION, Japan **INVITED**

The development of 3D structures is accelerating to overcome the limitations of lateral scaling in semiconductor devices. As for logic devices, for example, the introduction of the complementary field-effect transistors (CFET) is expected for the future scaling of SRAM cell areas and the improvement of device performance. As for memory devices, high aspect ratio (HAR) memory cells, vertical channel transistors and oxide semiconductors could help to realize a 3D memory device. These 3D architectures with advanced materials could outperform the current device performance and power efficiency.

To enable the complicated 3D structures as well those in 2D, ALD (atomic layer deposition) / AS-ALD (area selective atomic layer deposition) and ALE (atomic layer etching) are indispensable to manipulate the target thin films such as metal, metal nitride and metal oxide films. ALD is the technique to deposit atomically thin, smooth, and conformal films by making a chemical bond between a vapor phase precursor and a substrate surface irrespective of its topological complexity. AS-ALD is the kind of ALD process which can selectively deposit a target thin film on a target area of substrate based on surface chemical differentiation. AS-ALD has a lot of benefits including the elimination of etching processes and the reduction of cost. ALE is the technique to atomically etch a surface film by breaking chemical bonds in an isotropic or anisotropic manner followed by the formation of a volatile etch product. Although ALE is sometimes conceptualized as the opposite of ALD in terms of breaking and making chemical bonds, ALE / ALD are not reverse processes.

This tutorial will focus on the connection between precursor molecule design and ALD / AS-ALD and ALE processes. ALD precursors are basically metalorganic, inorganic and organic molecules. In most cases, they need to have a high vapor pressure, reasonable thermal stability, reactivity and high purity for high quality thin film deposition with an appropriate growth rate on a target substrate. The ALD process co-reactant can also be called an ALD precursor. It is not limited to O_2, H_2O, H_2 and NH_3 but may also be an organic molecule. AS-ALD precursors need to have a growth preference between a target growth area (GA) and non-growth area (NGA). In most cases of AS-ALD, we need an additional molecule such as a SAM (self-assembled monolayer) or SMI (small molecule inhibitor) to support the selective properties of the ALD precursor. ALE precursors are organic, inorganic, metalorganic molecules or their combinations. At the basic level, the ALE precursor, also called an etchant, needs to atomically react with a substrate surface to form a volatile by-product and to etch the surface monolayer.

In this tutorial, we will present and discuss how to design and select ALD / AS-ALD and ALE precursors with real life examples to help the audience deepen their understanding of precursor/thin film process relationships.

1:45pm **TS-SuA-4 Current and Future Perspectives on Atomic Layer Deposition**, ***W.M.M. (Erwin) Kessels***, Eindhoven University of Technology, Netherlands **INVITED**

Atomic layer deposition (ALD) has become one of the most influential thin-film deposition techniques of the past decades, enabling the synthesis of materials with atomic-scale control. By relying on self-limiting surface reactions, ALD offers precise thickness control, excellent uniformity and conformality on complex structures, and access to a wide range of materials. These capabilities have established ALD as a powerful platform for nanoscale materials engineering and an enabling technology across many areas of technology.

This tutorial will briefly revisit the fundamental principles of ALD. Particular attention will be given to the practical aspects of developing ALD processes, including a structured approach with practical steps that can be followed when designing and establishing ALD chemistries. The role of emerging data-driven approaches - including the potential use of AI to support process design and optimization - will also be addressed. As the field matures, the growing body of experimental ALD data is opening new opportunities for more systematic and data-driven approaches to materials discovery.

Building on this foundation, the tutorial will provide a perspective on the current state and future opportunities of ALD as a platform for materials synthesis. While the number of reported ALD processes continues to grow, many technologically relevant materials remain challenging to realize. These challenges include the deposition of new material systems such as 2D materials, the control of film properties at extremely small thicknesses, and the synthesis of ultrathin crystalline materials with well-defined properties.

The tutorial will also place ALD in the broader context of atomic-scale processing, highlighting its complementarity with related approaches such as atomic layer etching (ALE) and area-selective deposition (ASD). Together, these perspectives illustrate how ALD continues to expand its role as a key platform for engineering materials with atomic-level precision.

2:30pm **TS-SuA-7 Current and Future Perspectives on Atomic Layer Etching**, ***Thomas Tillocher***, GREMI - Orleans University - CNRS, France **INVITED**

Atomic Layer Etching (ALE) has been extensively studied these last years for microelectronic processes where high precision is required. ALE is a sequential process based on the self-limiting adsorption of reactive radicals on the first monolayer(s) of the material to be etched (“modification step”). Then, the modified layer is removed selectively to the pristine material under a low energy ion bombardment (“removal step”). This step is also self-limiting, as it stops when the modified layer is cleared, and since the ion energy is set just below the sputtering threshold of the pristine layer. By repeating the cycle, the material is etched one (or a few) monolayer(s) by one (or a few) monolayer(s). Plasma ALE is usually performed in standard ICP etching tools equipped with a gas injection system using fast ALD valves, designed to switch quickly from one gas to another.

For dielectric materials such as SiO_2 and Si_3N_4, ALE is usually achieved at room temperature of the substrate, and the modification step involves a C_4F_8 plasma. Sequential etching has been demonstrated but, this also leads to fluorocarbon deposition on the reactor walls, and eventually to process drifts, which affects reproducibility. Consequently, periodic chamber cleaning is necessary. Cryogenic ALE (Cryo-ALE) has been developed to address this limitation as well as to reduce material damage.

Plasma cryogenic etching consists in cooling the substrate to a temperature generally below -90°C, which significantly increases the surface residence time of adsorbed species. This enhances mechanisms such as passivation, physisorption, condensation or contributes to reduce plasma-induced damage as well chamber wall contamination. Therefore, Cryo-ALE is an ALE process operated at cryogenic temperature of the substrate. Two approaches have been developed and studied for SiO_2, Si and/or Si_3N_4: one where the modification is based on physisorption and the other is based on selective deposition.

This tutorial will first present the basics and the current status of ALE, as well as examples of applications. Next, as a perspective, the interest of cryogenic etching will be discussed.In particular, both physisorption and deposition-based Cryo-ALE processes will be presented: their principle, how they can be implemented and typical results will be described.

3:30pm **TS-SuA-11 Current and Future Perspectives of Area-Selective Deposition**, ***Han-Bo-Ram Lee***, Incheon National University, Republic of Korea **INVITED**

The technological evolution of the silicon industry is shifting from a design-driven era to a nanofabrication-driven era as physical limitations in nanofabrication become increasingly severe in the few-nanometer regime. At the same time, market demand continues to grow rapidly, driven not only by traditional computing and smartphone applications but also by emerging fields such as artificial intelligence and electric vehicles. Consequently, the role of semiconductor foundries, supported by new technological enablers, is becoming more critical than ever.

Area-selective deposition (ASD), based on atomic layer deposition (ALD), has attracted significant attention because it enables bottom-up patterning in three-dimensional structures without the complex etching and lithography processes required in conventional nanofabrication. While ASD has been highlighted for specific applications, such as mitigating edge placement error (EPE), it also holds significant potential for a wide range of semiconductor device applications. However, the practical implementation of ASD is strongly dependent on company-specific device architectures and process schemes, and therefore detailed information has not been widely shared within the research community.

Given the high level of complexity involved in semiconductor device fabrication, broader discussion and idea exchange within the research community could further accelerate technological development. In this tutorial, the fundamental principles of ASD, including the kinetics of nucleation and film growth as well as theoretical interpretations, will be introduced. This will be followed by case studies demonstrating the application of ASD in semiconductor devices. Several examples covering different device structures—such as logic, DRAM, and NAND—will be discussed to illustrate where and how ASD can be effectively utilized in production-level semiconductor device manufacturing.

4:15pm **TS-SuA-14 Atomic Layer Deposition from Lab-to-Fab*, Paul Poodt,*** SparkNano and Eindhoven University of Technology, Netherlands **INVITED**

Atomic Layer Deposition (ALD) has matured from a laboratory technique into a key enabling technology for industrial manufacturing across a broad range of applications. While new and diverse use cases for ALD continue to emerge, translating its inherent advantages (atomic-scale control, conformality, and uniformity) into cost-effective, high-throughput production remains a complex and strongly application-dependent challenge.

This tutorial addresses the industrialization and up-scaling of ALD, focusing on the practical trade-offs that govern throughput, cost of ownership, and precursor utilization. Different reactor concepts, process strategies, and integration approaches are examined to demonstrate why no universal solution exists for scalable ALD. Instead, successful implementation requires careful alignment of process design, equipment architecture, and manufacturing constraints with the specific requirements of each application.

Building on these lessons, the tutorial looks ahead to emerging challenges and opportunities associated with new ALD use cases. Topics include low-footprint processes, advanced process control for porous and high-surface-area substrates, extreme high-volume ALD for mass manufacturing, and the importance of precursor efficiency and large-scale precursor supply. The role of advanced modelling and predictive tools (including artificial intelligence and machine learning) combined with advanced metrology will be discussed. These capabilities are expected to play a critical role in how future ALD processes are developed, optimized, and deployed.

Most new ALD applications have humble beginnings though, often in a laboratory, in the hands of a student. The tutorial will conclude by illustrating how, even at this early stage, thoughtful process and materials choices can lay the foundation for scalable, sustainable, and economically viable future ALD applications.

5:00pm **TS-SuA-17 Advances in Spectroscopic Ellipsometry for ALD and ALE Thin Film Characterization*, Jeremy Van Derslice,*** J. A. Woollam Co., Inc.*; Greg Pribal, James Hilfiker,* J.A. Woollam Co., Inc. **INVITED**

Ellipsometry is a non-destructive optical technique that measures changes in the polarization state of light upon reflection from a surface, enabling determination of thin-film thickness and optical properties. Ellipsometry is sensitive to angstrom-level changes in film thickness and is therefore well suited to ALD and ALE, where it is used to monitor the cycle-by-cycle evolution of deposited or etched films and to determine growth or etch rates, identify growth windows, and evaluate film quality. This tutorial will introduce the principles of ellipsometry and show how the technique is conventionally used for ALD/ALE applications, from basic thickness determination to optical modeling of multilayer process stacks. We will then highlight three current topics relevant to the ALD/ALE community. First, we will discuss the use of artificial intelligence and other computational tools for automated model generation and parameter fitting. These tools are designed to reduce the level of expertise needed to interpret ellipsometry data. Second, we will examine modeling concepts for metallic films whose optical properties, specifically the free carrier parameters, vary as a function of thickness, which creates challenges for data interpretation. Third, we will introduce infrared ellipsometry using our new QCL-based IR-VASE platform, which enables high-speed IR measurements that provide insights into the chemistry involved in deposition and etch processes. By combining fundamentals with emerging methods, this tutorial will provide practical guidance for using ellipsometry in next-generation ALD/ALE applications.

Plenary Session
Room HB Plant Ballroom - Session PS1-MoM

Plenary Session

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

8:45am **PS1-MoM-1 ALD Welcome and Introductory Remarks***,*

9:00am **PS1-MoM-2 ALD Plenary Lecture: A Legacy of Atomic–Scale Innovation - Powering the AI Era***, Gurtej S. Sandhu,* Micron Technology **INVITED**

A commitment to innovation and creativity is required to meet demands of the new data age. These innovations help fuel the next generation of capabilities in Artificial Intelligence (AI) and enable technologies such as self-driving cars, smart medicine, industrial automation, space exploration etc. which sounded like science fiction not so long ago. The rapid rise of AI is reshaping computer architectures and placing unprecedented demands on memory performance and power efficiency. Memory has emerged as a critical enabler of modern AI systems, transforming memory from a supporting component into a central driver of system innovation.

This plenary talk explores how a legacy of atomic–scale process innovation has laid the foundation for today's AI memory era. Early adoption of atomic layer deposition (ALD) enabled key breakthroughs in memory scaling, establishing precision engineering as a strategic advantage that continues to scale with rising complexity. As chip complexity has been increasing exponentially, atomic–layer processes have become indispensable, enabling new device structures, tighter tolerances, and manufacturable solutions at extreme dimensions. In addition, there is need for advanced AI modeling tools to help engineers make informed decisions for building process flows faster, with less empirical experimentation. Traditional modeling however, has not kept up with pace and efficiency required for practical solutions and a unified approach across all facets of chip ecosystem and multi-disciplinary collaboration is needed. These solutions will require new breakthroughs in data processing and computational capabilities to enable more efficient and powerful multiscale modeling using advanced AI and physics-based approaches. By combining atomic–scale manufacturing with physics–based modeling and AI–driven insights, the industry is accelerating learning, reducing risk, and enabling faster innovation. Together, these capabilities are defining how memory will power the next era of AI.

Take–home message: *In the AI era, competitive advantage will belong to those who master atomic–scale manufacturing and amplify it with AI–driven technology development—turning complexity into speed, scale, and leadership.*

9:45am **PS1-MoM-5 ALD 2026 Innovator Awardee Talk: Atomic-Scale Engineering of Oxide Semiconductors by ALD: From Display Innovations to Semiconductor Channel Platforms***, Jin-Seong Park,* Hanyang University, Korea **INVITED**

Oxide semiconductors have transformed modern display backplanes by enabling high-performance thin-film transistors (TFTs) with low leakage current and low-temperature process compatibility. Yet extending oxide semiconductors from large-area electronics into semiconductor memory/logic introduces a new set of constraints—three-dimensional topography, stringent variability control, interface-limited transport, and integration-driven reliability requirements that are not easily met by conventional deposition schemes. Atomic layer deposition (ALD), with its self-limiting surface reactions, offers a unique pathway to address these challenges through conformal film growth on high-aspect-ratio structures and atomic-level control over thickness, composition, and interfaces.

In this plenary talk, I will present the evolution of my ALD research from display technologies—starting with OLED thin-film encapsulation and extending to oxide TFT channel/dielectric engineering—toward semiconductor channel applications based on ALD-grown oxide semiconductors. The discussion will focus on three practical "atomic-scale levers" that enable this transition. First, composition and stacking-sequence control in multi-cation oxides, using ALD super-cycles to tune carrier transport and uniformity. Second, crystallinity and defect management, where the balance between mobility and stability is engineered by controlling phase evolution and oxygen-related defects across nanometer-scale films. Third, interface and integration engineering—including dielectric/channel and contact interfaces, thermal budget considerations, and hydrogen-related reliability—aimed at compatibility with vertically integrated memory architectures. Finally, I will outline a forward-looking roadmap in which atomic layer processes—combining ALD with selective interface modification and, where appropriate, atomic layer etching—provide manufacturable routes for oxide semiconductor channels in future 3D systems. By connecting display-validated ALD know-how to semiconductor integration demands, this talk will highlight how ALD oxide semiconductors can emerge as a scalable channel platform for the next era of vertically integrated electronics.

Plenary Session
Room HB Plant Ballroom - Session PS2-MoM

ALE Plenary Session

Moderators: Nathan Marchak, IBM, **Christophe Vallée**, University of Albany

10:45am **PS2-MoM-9 ALE Welcome and Introductory Remarks***,*

11:00am **PS2-MoM-10 ALE Plenary Lecture: From Atoms to Systems: Atomic-Layer Engineering for the Next Era of Logic and Memory Technologies***, Gaurav Thareja,* AMAT **INVITED**

ALD Applications

Room Ybor Salons I-IV - Session AA-MoA

Quantum ALD Applications

Moderators: Robert Clark, TEL Technology Center, America, LLC, **Arpita Saha**, Oxford Instruments

4:00pm **AA-MoA-11 Two Level Systems Mitigation by Atomic Layer Deposition for Quantum Application**, ***Thomas Proslier***, *Yasmine Kalboussi, Théo Dejob, Fabien Eozenou, Gregoire Jullien,* CEA Saclay, France*; sandrine Tusseau-nenez,* Ecole Polytechnique - CNRS, France*; Nathalie Brun, Michael Walls,* Université Paris-Saclay, France*; frédéric miserque, Maurice Luc,* CEA Saclay, France **INVITED**

Superconducting quantum bits (qubits) are regarded as one of the key technological building blocks for future quantum computers and sensors. One of the primary obstacles to extending qubit performance and in particular their coherence times is the presence of photon-absorbing defects, commonly modeled as two-level systems (TLS). Microscopic sources of TLS—such as oxygen vacancies, hydroxyl groups, and amorphized structures—have been identified in dielectric surfaces, interfaces, and Josephson junctions. Thanks to its atomic-scale control of composition and thickness, atomic layer deposition (ALD) offers a powerful approach to address this challenge and mitigate some of these defects mechanisms. ALD is also fully compatible with standard microelectronic fabrication processes and can be readily integrated into the production of two-dimensional superconducting films.

Niobium (Nb) superconducting cavities, widely used in particle accelerators, provide a simpler type of resonator compared to qubits, with the advantage of involving only a single interface—Nb and vacuum. This makes them ideal platforms for investigating how the structure, chemical composition, and thickness of various oxide capping layers affect resonator performance and TLS properties.

I will present performance measurements from Nb superconducting resonators coated via ALD with amorphous as well as crystalline films with thicknesses between 2 and 10 nm. Following thermal treatments, these coatings were found to enhance quality factors and coherence times relative to bare niobium with its native oxide. TLS-model fits of RF measurements, combined with surface characterization techniques such as XPS and TEM, enable the extraction of TLS properties—including dielectric losses and defect concentrations—in the various capping layers.

These findings offer valuable insight for future technological developments of superconducting resonators operating in the quantum regime, including qubit architectures.

4:30pm **AA-MoA-13 Atomic Layer Deposition Based Dopant Engineering of Er-Doped CeO_2 Thin Films for Scalable Quantum Materials**, ***Terrick McNealy-James,*** University of Central Florida*; Emily Miura-Stempel, Ratul Mangalr,* University of Washington*; Justin Moore, Diego Javier-Jimenez, Titel Jurca,* University of Central Florida*; Brandi Cossairt,* University of Washington*; Parag Banerjee,* University of Central Florida

Quantum information technology has the potential to transform sensing, communication, and computing by exploiting intrinsic spin-photon interfaces of rare-earth-ions (REIs). These spin-photon interfaces stem from the shielded 4f-shell electrons of REI's, which give rise to long-lived electron spin states and long coherence times. When combined with the compatibility of solid-state dielectric host materials with established silicon-based integration and fabrication technologies, REI's can become a promising pathway towards developing scalable solid-state quantum platforms.

Among the candidates for host materials, cerium oxide (CeO_2) is an attractive option with its crystalline morphology, wide band gap (3.19 eV) and low concentration of nuclear spins, all of which contribute to reduced magnetic noise and a theoretically predicted coherence times of up to 47 ms. Building on these characteristics, erbium-doped cerium oxide ($Er:CeO_2$) has become a compelling solid-state material for spin-based quantum information processing. Studies of $Er:CeO_2$ nanoparticles have demonstrated long electron spin coherence times in the microsecond range. However, the morphology and particulate nature of nanoparticles present a significant challenge for large scale integration into solid-state device architectures.

In this work, we address these challenges by developing $Er:CeO_2$ thin films via atomic layer deposition (ALD), a gas phase, wafer scale technique capable of angstrom-level thickness control, conformal coating, and precise dopant incorporation. Two distinct ALD based doping strategies are investigated and compared. The first approach uses a super cycle method, in which Er_2O_3 cycles are periodically inserted into CeO_2 growth sequence to control dopant concentration through cycle ratio adaptations. The second, less-explored approach utilizes co-dosing of erbium and cerium precursors in the same ALD cycle with the goal of achieving a more spatially dispersed dopant distribution.

To establish an understanding of each doping strategy dual and tandem techniques of *in situ* quadrupole mass spectrometry (QMS) and spectroscopic ellipsometry (SE) are used to monitor film growth behavior and gas-phase reaction chemistry during deposition. *Ex situ* techniques including x-ray photoelectron spectroscopy (XPS), x-ray diffraction (XRD), and Raman spectroscopy are used to correlate dopant incorporation pathways with structure-property relationships. Additionally, pump-probe spectroscopic techniques will measure the lifetimes of the spin polarized electrons in $Er:CeO_2$ and benchmark their performance to state-of-art, spin-photon systems.

4:45pm **AA-MoA-14 Superconducting Nitrides by Fast Remote Plasma ALD for Quantum Applications**, ***Harm Knoops,*** *Arpita Saha, Dmytro Besprozvannyy, Nick Chittock,* Oxford Instruments Plasma Technology, UK*; Silke Peeters, W.M.M. (Erwin) Kessels,* Eindhoven University of Technology, Netherlands*; Ciaran Lennon,* Oxford Instruments Plasma Technology, UK*; Nidhi Choudhary, Robert Hadfield,* University of Glasgow, UK*; Iliya Shiravand, Davood Shahrjerdi,* New York University*; Christos Zachariadis, Alessandro Bruno,* QuantWare B.V., Netherlands

Superconducting films ranging from a few to hundreds of nanometers are at the basis of a wide range of quantum devices and are therefore key in advancing quantum technology to an era of widespread utility. The further development of quantum technologies hinges on improvements in materials and their interfaces using scalable processing. With its atomic-scale growth control and wafer-scale uniformity, plasma-enhanced ALD (PEALD) could become an enabling technique for the growth of superconducting thin films with high-quality interfaces. High-throughput processes would facilitate the growth of films beyond the few tens of nanometers, broadening the application perspective for ALD of superconducting films.

We demonstrate PEALD including substrate biasing for a variety of superconducting nitride films ranging from 5 to 100 nm thickness, with a high throughput of up to > 50 nm/houron the PlasmaPro ASP system. The nitrides TiN, NbN, NbTiN, and TaCN are deposited and investigated through a range of collaborations with the intent to show their utility for quantum device applications.

Extensive material analysis shows how NbN, TiN, and NbTiN have useful film properties and remain superconducting down to low thicknesses.[1,2] Substrate biasing during PEALD enables tuning of the materials properties either by reducing contaminants in the film and improving crystallinity to achieve low resistivities, or by increasing disorder for applications such as microwave kinetic inductance detectors. For Nb and Ta compounds the presence of carbon is interesting in that it can be present in the form of superconducting carbonitrides (shown for Nb and Ta compounds).[2,3] Furthermore, these carbonitride films were found to support high internal quality factors exceeding 10^5 at 50 mK in the single-photon regime.[3]

The wide parameter space enabled by PEALD was also found to allow for high-quality planar TiN films. As an example, two samples achieved a T_c of 4.583 ± 0.005 K and 4.700 ± 0.005 K respectively with a narrow transition width of 0.007 ± 0.003 K indicating high material quality with minimal contamination. Further collaboration with partners is ongoing to showcase the utility of these films in 3D structures as through-silicon vias. Here several mA of critical current was found per via in preliminary work. These and other results indicate the promise of superconducting nitrides by fast remote plasma ALD for quantum applications.

1. Peeters et al., *AVS Quantum Sci.* **7**, 026801 (2025)

2. Choudhary et al., *APL Mater.* **13**, 111104 (2025)

3. Shiravand et al., *Appl. Phys. Lett.* **127**, 192603 (2025)

5:00pm **AA-MoA-15 Wafer-Scale Thermal ALD of Superconducting TiN: A Scalable Process with Room-Temperature Predictive Mapping**, ***Sanaz Zarabi,*** *John Rönn, Otto Laitinen,* Beneq Oy, Finland

Superconducting thin films are at the heart of next-generation technologies, from quantum computing to ultra-sensitive detectors, but their integration into scalable microfabrication remains a bottleneck. Titanium nitride (TiN), with its tunable superconducting properties and compatibility with CMOS processes, stands out as a key material candidate (1-2). In this work, we report a fully thermal ALD process for TiN deposition

on 200 mm wafers using $TiCl_4$ and NH_3 at **480 °C** with **TFS200** reactor, achieving homogeneous films with a superconducting critical temperature (Tc) of **3.65 K** with an average thickness of **45.23 nm,** shown in Figure 1. Importantly, the process is directly scalable to a batch process without degradation in superconducting performance, maintaining a thickness non-uniformity (σ/avg) of **4.34 %**.

To tackle the longstanding limitation of cryogenic, localized T_c measurements, we introduce a non-destructive room-temperature metrology strategy for the first time that correlates **refractive index and extinction coefficient** (measured via **spectroscopic ellipsometry**) with superconducting behavior. This enables rapid, full-wafer assessment of superconductivity without using cryogenic equipment, providing a powerful tool for both process monitoring and device screening. Using this method, we quantify superconductivity non-uniformity (σ/avg) across a 200 mm wafer with 5 mm edge exclusion to be **1.87%** for single-wafer deposition and **1.21%** in batch processing, validating the approach as a powerful tool for scaling superconducting materials into manufacturable device platforms.

Furthermore, we present comprehensive structural and compositional characterization using **TEM**, **XRD**, and **ToF-ERDA** to probe grain structure, crystallinity, stoichiometry, and impurity content. These insights directly link film quality to superconducting behavior, deepening our understanding of how to optimize ALD-grown TiN for quantum and cryogenic applications.

Together, these results establish a scalable, high-performance route to superconducting TiN, backed by both advanced characterization and a practical, predictive metrology framework tailored for real-world manufacturing.

References:

1. Deyu, Getnet Kacha, Marc Wenskat, Isabel González Díaz-Palacio, Robert H. Blick, Robert Zierold, and Wolfgang Hillert. "Recent advances in atomic layer deposition of superconducting thin films: a review." *Materials Horizons* (2025).
2. Grigoras, Kestutis, N. Yurttagül, J-P. Kaikkonen, Elsa T. Mannila, Patrik Eskelinen, D. P. Lozano, H-X. Li et al. "Qubit-compatible substrates with superconducting through-silicon vias." *IEEE Transactions on Quantum Engineering* 3 (2022).

5:15pm **AA-MoA-16 ALD Outstanding Presentation Award Finalist: Growth of Superconducting Trilayer NbN/AlN/NbN Structures for Photonics and Quantum Computing Applications***, **Ciaran Lennon,*** Oxford Instruments Plasma Technology, UK*; Nidhi Choudhary,* University of Glasgow, UK*; Dmytro Besprozvanny,* Oxford Instruments Plasma Technology, UK*; Valentino Seferai,* University of Glasgow, UK*; Arpita Saha,* Oxford Instruments Plasma Technology, UK*; Harm Knoops,* Oxford Instruments Plasma Technology, Netherlands*; Harriet van der Vliet,* Oxford Instruments Plasma Technology, UK*; Robert Hadfield, Martin Weides,* University of Glasgow, UK

Superconducting materials are the building blocks for many nascent quantum technologies that underpin the quantum revolution of the 21st century. Reliable and reproducible growth of superconducting materials, particularly thin films, is paramount for the ongoing progress of the field [1,2]. Plasma-enhanced atomic layer deposition (PEALD) has recently been demonstrated as a promising candidate for superconducting thin film growth, offering superior uniformity, conformality and thickness control to conventional physical vapor deposition techniques, such as sputtering, while exhibiting superior film quality (T_c and J_c) and more compositional variety than thermal ALD [3]. Critically, the role of RF substrate biasing in PEALD of superconducting thin films, allowing for greater ion energy control, has also been shown to improve the superconducting properties and provide more tunability for specific device applications [4,5].

Owing to the sub-nm thickness control and compositional diversity of PEALD, allowing for growth of relatively complex heterostructures, we have identified it as the ideal technique for the growth of superconducting multilayer structures for both superconducting nanowire single-photon detectors (SNSPDs) and Josephson junctions (JJs) [6]. Our work presents a study of the growth of NbN/AlN/NbN trilayer structures using PEALD with RF substrate biasing, with 5 nm NbN layers (SNSPDs) and 30 nm NbN layers (JJs), detailing their structure, morphology, composition and superconducting properties. We report T_c > 6 K for 5 nm NbN layers and T_c > 12 K for 30 nm layers. We then present the fabrication of both multilayer SNSPD and JJ structures using electron beam lithography and reactive ion etching. For the multilayer SNSPDs, we present device characterization from 1.5 µm up to 4 µm wavelengths, examining the device performance in the mid-IR. For the JJ structures we present preliminary results detailing the electrical properties, including the critical current density (J_c), of devices tested at millikelvin temperatures.

Overall, this work presents significant progress in the development of a PEALD toolbox for the growth of high-quality superconducting multilayer structures for the development of a variety of superconducting quantum device modalities.

[1] Morozov D. V., et al., Contemp Phys **62** 69–91

[2]de Leon N. P., et al., Science **372** 253

[3]Peeters S. A., et al., Appl Phys Lett **123** 132603

[4]Lennon C. T., et al., Materials for Quantum Technology **3** 045401

[5] Wang D., et al., Nature Materials https://doi.org/10.1038/s41563-025-02448-

[6]Alam S., et al., Coatings **13** 278

ALD Fundamentals: Growth and Characterization
Room HB Plant Ballroom - Session AF-MoA

ALD Precursor Design I

Moderators: Rick Chen, The Electronics business of Merck KGaA Darmstadt, **Atsushi Sakurai**, ADEKA CORPORATION

4:00pm **AF-MoA-11 Bridging Code and Chemistry: The Origin of Precursor Decomposition***, **Seungjin Song**, Ga Youn Lee, Dexter Dimova, Sean Barry,* Carleton University, Canada

Yttrium (Y) and scandium (Sc) play critical roles in high-k material by forming Y_2O_3 and Sc_2O_3 high-k dielectric oxides, so that they can suppress leakage current and improve thermal stability in advanced semiconductor devices. Conventional Cp- and β-diketonate-based precursors suffer from limitations such as high deposition temperatures, low surface reactivity, and carbon contamination. Therefore, the development of next-generation Y and Sc precursors with high volatility, strong reactivity, and low impurity incorporation is essential for future nanoscale device fabrication.

Our group uses a silicon-containing ligand to prepare the homoleptic Y and Sc precursors and investigates the origin of thermal decomposition in precursors containing highly basic ligands. We synthesized the homoleptic group 3 precursor using salt metathesis and acid-base reaction. Our product was characterized through nuclear magnetic resonance (NMR) spectroscopy and single-crystal X-ray diffraction (SC-XRD). We investigated the thermal properties of the complex by thermogravimetric analysis and, using flame-sealed samples in a glass tube, revealed the origin of the thermal decomposition mechanism by NMR spectroscopy and density functional theory (DFT) calculations with Eyring analysis.

Our DFT calculations and Eyring analysis allow us to identify the key structural point in the precursors to prevent thermal decomposition. This talk will focus on connecting the experimental observations and DFT calculations through the Eyring analysis. The presentation will show a detailed synthesis and characterization, and mechanistic thermal decomposition pathways for a representative methodology on how we connect the DFT calculations and experimental observations.

4:15pm **AF-MoA-12 Multi-Objective Discovery of New Precursors for ALD with Steerable Generative AI***, **Tristan Deleu,*** Entalpic, Canada*; Alexandre Duval,* Entalpic, France

Advances in atomic layer processes are often constrained by the limited availability of precursors that satisfy an increasingly complex set of requirements for the deposition of specific thin films. The development of novel precursors for ALD poses unique challenges in organometallic chemistry, where ideal candidates must balance multiple objectives simultaneously. For example, they must be stable at room temperature for safe storage in liquid form and possess a volatility range that matches the optimal ALD temperature window, all while guaranteeing proper reaction with the substrate to avoid contamination. While historically the design of new compounds has often relied on experience and chemical intuition, there is now an opportunity to leverage modern tools from artificial intelligence (AI) to navigate this massive chemical space at scale and accelerate discovery.

At Entalpic, we are building a platform that applies cutting-edge generative AI to find a wide range of new candidate precursors. Our approach integrates a collection of prediction models, each of them targeting desirable properties for ALD, to steer our generative models towards molecules of interest within a multi-objective optimization framework. We first train a general-purpose model capable of generating organometallic

complexes, based on open-data available through initiatives such as LeMaterial. Depending on controllable settings, the model can either construct new molecules from an existing library of ligands available for purchase, or discover new ligands altogether while ensuring synthesizability of the final complexes.

Recognizing that ligands in transition metal complexes play an essential role in determining their properties, we train a variety of machine learning (ML) models, such as transformers, graph neural networks (GNNs), and machine learning interatomic potentials (MLIPs), to accurately predict vapor pressure and other critical parameters, while ensuring robust generalization to new ligands. These predictive models then provide a feedback signal to guide our pre-trained generative model with reinforcement learning (RL). Finally, these molecules suggested by the fine-tuned generative model undergo a series of thermodynamic screening steps to narrow down the set of promising candidates that can be submitted to the lab for evaluation.

4:30pm **AF-MoA-13 First-Principles Screening of Precursors and Inhibitors to Achieve Enlarged-Grain MoS_2 Through Area-Selective Deposition**, ***Bram van der Linden,*** KU Leuven and Imec, Belgium*; Geoffrey Pourtois, Sergiu Clima,* IMEC, Belgium*; Ian Campbell,* IMEC*; Pierre Morin, César Javier Lockhart de la Rosa,* IMEC, Belgium*; Ageeth Bol,* University of Michigan, Ann Arbor*; Annelies Delabie,* KU Leuven and Imec, Belgium

MoS_2 is a promising channel material for field-effect transistors, owing to its superb intrinsic carrier mobility at nanoscale dimensions. While Atomic Layer Deposition (ALD) enables conformal deposition of MoS_2, it typically yields nanocrystalline layers with low mobility due to grain-boundary scattering. Enlarged MoS_2 grain sizes are essential to obtain the mobility needed for nano-electronic devices. This may be achieved through inhibitor molecules that passivate part of the reactive groups at the initial surface, thus reducing the number of sites available for nucleation. The vast number of possible precursor-inhibitor combinations makes experimental assessment too time-consuming and costly. We therefore use first-principles thermodynamic simulations to evaluate the two most important criteria for achieving large MoS_2 grain sizes using surface inhibitors: highly reactive molybdenum precursors and sulfur co-reactants, and effective surface inhibitors that block adsorption of the molybdenum precursors and sulfur co-reactants.

To enable efficient screening of precursors and inhibitors, we developed a three-step first-principles thermodynamic approach. Using this framework, we assess the reactivity of 14 molybdenum precursors reported for the growth of various molybdenum-based materials, with H_2S as the sulfur source. The precursor reactivity is evaluated in combination with 15 SiO_2 surface (passivation) chemistries under typical low–temperature ALD conditions (200°C, 0.1Torr). First, we evaluate the thermodynamic driving force for each precursor to form monolayer-thin MoS_2 crystals of various sizes. $Mo(NMe_2)_4$ is the only precursor that exhibits strong thermodynamic driving forces for forming all tested grain sizes, consistent with the low ALD growth temperature (60°C) reported for this precursor[1]. For all precursors, reactivity improves with increasing grain size. In addition, we could identify new promising precursors for MoS_2 ALD, such as $MoCl_4O$. Second, we use a SiO_2 cluster model to calculate the reaction energies of molybdenum precursors and H_2S with the reactive surface hydroxyl groups and candidate surface-passivation groups. -Si-F emerges as one of the most promising surface passivation groups, as precursor reactions yield largely endothermic reaction energies, suggesting strong inhibition of MoS_2 growth. Third, to verify the results of the SiO_2 cluster approach, we compute the reaction energies for selected precursor-inhibitor combinations using a periodic SiO_2 surface slab model. The combined use of cluster and slab models enables efficient screening of precursors and inhibitors, ultimately identifying promising ALD process conditions that yield films with enlarged MoS_2 grains.

(1) T. Jurca et al. Low-Temperature Atomic Layer Deposition of MoS_2 Films. *Angew Chem Int Ed* **2017**, *56* (18), 4991–4995.

4:45pm **AF-MoA-14 Molecular–Level Insight Into Thermal Stability and Substrate–Dependent Nucleation of DDAP for Platinum ALD**, ***Tomohiro Tsugawa,*** *Hideaki Nakatsubo, Yohei Kotsugi, Ryosuke Harada,* TANAKA PRECIOUS METAL TECHNOLOGIES Co., Ltd., Japan

Platinum (Pt) thin films are widely utilized in advanced semiconductor devices due to their low resistivity, high work function, catalytic activity, and excellent thermal stability. Atomic layer deposition (ALD) of Pt is essential for achieving film thicknesses below 20nm with superior conformality in high–aspect–ratio 3D structures. However, stable and uniform Pt–ALD remains difficult because conventional precursors exhibit limited thermal stability, insufficient volatility, and substrate–dependent nucleation behavior that is not yet fully understood.

In this work, we investigate the Pt precursor DDAP (Dimethyl-(3,4–*η*)-*N*,*N*–dimethyl–3–butene–1–amine–*N*)platinum(II), $C_8H_{19}NPt$), which has demonstrated high ALD growth rates and low–resistivity Pt films using O_2 as a reactant [1, 2]. Despite its promising performance, the molecular–level origins of its thermal stability and substrate–specific growth characteristics have remained unclear. We present a combined experimental and simulation study such as density functional theory (DFT) to clarify these mechanisms.

DFT analysis identifies intrinsic thermal decomposition pathways and activation barriers consistent with the experimentally observed onset of precursor decomposition near 275 ℃, providing mechanistic insight into the established ALD process window. Furthermore, adsorption energetics were evaluated on technologically relevant surfaces including Pt, Cu, TiN, and oxide substrates such as OH–terminated SiO_2, Al_2O_3, and ZrO_2. DDAP exhibits weaker adsorption on oxide surfaces compared to metals, correlating with delayed nucleation and non–uniform initial Pt growth observed experimentally on SiO_2.

By linking ALD behavior directly to DFT–derived energetics, this study provides a molecular–level explanation for DDAP's thermal properties and substrate–dependent nucleation phenomena. These insights offer guidance for designing next–generation Pt precursors optimized for highly conformal and substrate selective ALD processes.

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5:00pm **AF-MoA-15 Theoretical Analysis on Organic Sulfur Sources for Atomic Layer Deposition of MoS_2**, ***Myeong Kyun Nam,*** Hongik University, Republic of Korea*; Bonggeun Shong,* Hanyang University, Republic of Korea

Molybdenum disulfide (MoS_2) is widely recognized as a promising two-dimensional semiconductor material. Atomic layer deposition (ALD) can provide a scalable route for the controlled synthesis of MoS_2. Conventional ALD processes of sulfides often employ H_2S as the sulfur source; however, its extreme toxicity has motivated development of benign alternative sulfur sources. Previous studies have reported MoS_2 ALD processes using organic sulfur precursors such as diethyl sulfide (DES) and diethyl disulfide (DEDS), in combination with $Mo(CO)_6$ as the molybdenum precursor [1]. Experimental results indicate that DEDS achieves higher growth rates and more efficient nucleation than DES [1]. In this work, density functional theory (DFT) and machine learning interatomic potential (MLIP) calculations are employed to elucidate the chemical reaction mechanisms and fundamental origins of the distinct reactivities of DES and DEDS during MoS_2 ALD. MoS_2 edge models with thermodynamically stable hydrogen coverages are constructed under appropriate temperature and pressure conditions. Adsorption of $Mo(CO)_6$ on these surfaces exhibits self-limiting behavior, consistent with the characteristics of ALD processes. Subsequent reactions with DES and DEDS are investigated with emphasis on the removal of residual CO ligands bound to surface Mo. Our results reveal that the cleavage of the S-S bond, present only in DEDS, is relatively facile in contrast to the cleavage of the C-S bonds. Current research could contribute to a deeper understanding of the chemistry behind sulfide ALD, and provides insights into utilization of organic reactants in ALD.

References [1] Adv. Mater. 29, 47, 1703031 (2017)

5:15pm **AF-MoA-16 A Data-Science Approach to the Analysis of Temperature-Dependent Alumina Atomic Layer Deposition Growth Per Cycle**, ***Raymond Adomaitis,*** University of Maryland

Temperature-dependent alumina atomic layer deposition (ALD) growth per cycle (GPC) data were collected from nearly 40 studies of the trimethylaluminum (TMA)/water ALD process. The data were used in multiple regression approaches based on fitting the data to globally defined polynomials in temperature T, and two linear piecewise-continuous representations of the fitted data, each patterned after the hypothesized existence of an ALD window exhibiting constant or linear GPC(T) dependence. All three regression approaches identified a low-T region characterized by rising GPC with T, reaching a maximum of approximately 1.1 A/cycle slightly below 200 deg. C, followed by a slower decline in GPC with T after this point. The results indicate that a temperature-independent ALD window for the TMA/water system may be relatively small (with lower and upper limits of 177 and 208 deg. C, respectively), if it exists at all.

Multiple approaches to statistical analysis of the validity of observed trends will be presented.

Reference

Adomaitis, R. A., "Regression analysis of temperature-dependent alumina atomic layer deposition growth per cycle using trimethylaluminum and water as precursors," J. Vac. Sci. Technol. A 43 062406 (2025) DOI: 10.1116/6.0004738

ALDALE

Room HB Plant Ballroom - Session ALDALE-MoA

Student Awards

Moderators: Parag Banerjee, University of Central Florida, **Nathan Marchak**, IBM

1:30pm **ALDALE-MoA-1 Physics-Informed Bayesian Active Learning Framework for Efficient Precursor Pulse Time Tuning in Atomic Layer Deposition***, **Pouyan Navabi**, Christos Takoudis,* University of Illinois - Chicago

ALD process development traditionally requires extensive trial-and-error experiments to identify optimal precursor pulse times that achieve saturation, consuming significant precursor material and machine time. We present a physics-informed Bayesian active learning framework that autonomously tunes precursor pulse times by integrating Langmuir adsorption kinetics directly into Gaussian process (GP) regression models.

Our methodology introduces a two-stage parameter estimation strategy that decouples noise filtering from physical parameter extraction. Rather than fitting Langmuir parameters directly to sparse, noisy measurements, we leverage the GP's smoothing capabilities by first generating dense, noise-free predictions, then fitting Langmuir parameters to the smoothed curves. This effectively separates signal from experimental noise while maintaining physical interpretability.

We systematically evaluate the framework across diverse saturation behaviors, including cases requiring extrapolation beyond explored parameter space and scenarios with elevated experimental noise. Compared to purely data-driven GP approaches, the physics-informed model demonstrates convergence within five iterations, up to fourfold improvement in prediction accuracy, and two to fourfold reduction in precursor consumption across all tested conditions. Experimental validation using TiO2 deposition via TDMAT and O3 with in situ SE confirms accurate identification of saturation times for high-coverage targets, with observed deviations at lower saturation levels providing valuable mechanistic insights into desorption behaviors.

Unlike neural network approaches requiring hundreds to thousands of datapoints for each precursor chemistry, our framework achieves accurate predictions with 5-10 iterations. While digital twin architectures provide powerful capabilities, they necessitate simultaneous implementation of computational models and control infrastructure, increasing complexity. Our approach requires only the learning algorithm and in situ measurement, enabling straightforward deployment.

Future work requires development of a generalized physical model incorporating desorption and etch factors with minimal tunable parameters to accurately predict low saturation regimes, which would enable precision composition control in supercycle ALD while maintaining film homogeneity. Extension to multi-parameter optimization and integration of sophisticated mechanisms would broaden applicability. The methodology's generalizability suggests extension to diverse ALD chemistries including metal-organic, halide, and plasma-enhanced processes. Hybrid approaches combining physics-informed priors with neural network flexibility could leverage both paradigms. Integration with emerging in situ characterization techniques and closed-loop control could enable fully autonomous reactor operation, accelerating materials discovery while minimizing environmental impact through reduced precursor waste.

1:45pm **ALDALE-MoA-2 To ALD or Not to ALD on Lithium? Controlling Growth Through Plasma Pretreatments***, **Tippi Verhelle**, Lowie Henderick, Siebe Coessens, Matthias Minjauw, Jolien Dendooven, Christophe Detavernier,* Ghent University, Belgium

Protective ALD coatings directly deposited onto metallic lithium have shown to be a promising strategy to improve the performance of lithium metal batteries. [1-2] Already a few studies report the successful deposition of Al_2O_3 on metallic lithium, however, there are very few who study the growth mechanism more in-depth. Moreover, previous reports often use as-received metallic lithium as a substrate, although it is well-known to contain a native oxide layer, consisting out of Li_2CO_3, LiOH and Li_2O. This surface composition can evolve over time, depending on the storage conditions [3], making it an unreliable starting surface for ALD growth.

To gain more control over the initial surface, we have explored plasma pretreatments in the same vacuum chamber as the ALD process, reducing the risk of recontamination. An argon plasma pretreatment results in removal of the native layer, leaving a mostly Li_2O-terminated surface, whereas an O_2 plasma treatment leads to a mixed LiOH/Li_2O surface termination. (Figure 1) Using in-vacuo X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM) without air-exposure, we were able to study the growth behavior of the trimethylaluminium (TMA) and O_2 plasma ALD process on these plasma pretreated lithium surfaces.

A TMA exposure of 30s on the Ar plasma-treated surface leads to uncontrolled precursor decomposition. In-vacuo XPS shows a combination of C, Al and Li (with the relative composition 46 at.% C, 32 at.% Li and 18 at.% Al) at the surface in the form of Li-Al and Al-C. Furthermore, SEM imaging shows that the decomposition layer quickly grows into a micrometer thick and porous layer. (Figure 2) This substantial decomposition behavior can be linked to the likely porous nature of the Li_2O layer (based on its Pilling-Bedworth-Ratio=0.57), allowing direct interaction between TMA and underlying metallic lithium.

In contrast, TMA exposure on an O_2 plasma pretreated surface results in self-limited reactions, clear from the TMA saturation behavior as measured with in-vacuo XPS. With increasing TMA-O_2 plasma ALD cycles, an Al_2O_3 peak in the O 1s spectrum becomes visible, meaning that the LiOH component is able to support initial ALD-like reactions for further Al_2O_3 growth. (Figure 3)

The findings presented in this work show the importance of a standardized pretreatment and the necessity for reporting the initial lithium surface state, in order to make comparison between future studies easier.

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2:00pm **ALDALE-MoA-3 Atomic Layer Deposition of Metallic Molybdenum Dioxide Thin Films Enabling High-k Rutile Capacitors***, **Alexey Ganzhinov**, Miika Mattinen, Marko Vehkamäki, Kenichiro Mizohata, Mykhailo Chundak,* University of Helsinki, Finland*; Georgi Popov,* ASM Microchemistry Ltd., Finland*; Mikko Ritala, Matti Putkonen,* University of Helsinki, Finland

Molybdenum dioxide (MoO_2) thin films have attracted considerable attention as electrode materials for high-*k* capacitors, such as those used in dynamic random-access memory (DRAM) devices. This is especially relevant now, as emerging AI applications have already multiplied demand and prices of DRAM memory. The properties that make MoO_2 highly attractive include high conductivity, high work function (>5 eV), distorted rutile crystal structure, and chemical stability. However, deposition of crystalline MoO_2 thin films have proven challenging as molybdenum oxides possess multiple oxidation states (Mo^{4+}, Mo^{5+}, Mo^{6+}) as well as myriad of different phases (α-, β-MoO_3, Magnéli phase suboxides... etc.), with α-MoO_3 being the most stable polymorph. Hence, currently atomic layer deposition (ALD) of crystalline MoO_2 thin films is not possible without additional (post-)deposition steps.

For modern DRAM devices, it is integral that new materials are deposited using ALD, as it is the only technique that offers perfect conformality on complex 3D structures with extremely high aspect ratios. Here, we present first direct ALD process for crystalline MoO_2 thin films using molybdenum(II) acetate dimer ($Mo_2(OAc)_4$) and oxygen (O_2) as precursors. The process yields crystalline MoO_2 films with distorted rutile (tugarinovite) crystal structure at 235-275 °C. The films were stoichiometric, exceptionally pure with ~1 at.% total impurities, and highly conductive with a resistivity of 400 μΩ·cm. The growth rate of the process ranges from 0.1 to 1.6 Å/cycle, depending on the deposition parameters. This process expands the selection of molybdenum oxides that can be deposited by ALD with MoO_2, making it possible to deposit thin films from MoO_2 to $MoO_{x<3}$ to MoO_3.

To demonstrate applicability of our process for high-*k* capacitors, we show that phase of titanium dioxide (TiO_2) shifts from anatase (*k*~25-50) to rutile (*k*~90-170) when it is deposited on top of MoO_2 at low temperatures (150-275 °C). Subsequently, we use this effect to deposit high-*k* capacitor devices, confirming great potential of the process and MoO_2 as a solution for next-generation DRAM electrodes.

2:15pm **ALDALE-MoA-4 Atomic Layer Deposition of Ultrathin Topological Semimetals with Thickness-Dependent Resistivity**, ***Yea-Ji Kim***, *Il-Kwon Oh, Ae Rim Choi,* Ajou University, Republic of Korea*; Thi-Kim Hue Dinh, Bui-Nhat Le Dang,* Ajou University, Viet Nam*; Hyun-Mi Kim,* Korea Electronics Technology Institute, Republic of Korea*; Asir Intisar Khan,* UC Berkeley EECS, Bangladesh

As the device dimension continues being scaled down, conventional interconnect metals suffer from severe performance degradation at reduced thicknesses, motivating the search for alternative materials compatible with advanced integration schemes. Topological semimetals (TSMs) have recently emerged as promising candidates due to their unconventional transport behavior in the ultrathin regime. [1] For example, prior studies on NbP and TaP have shown that these Weyl semimetals exhibit robust metallic transport and suppressed resistance degradation. [2], [3] We recently published to Science, demonstrating that ultrathin non-crystalline NbP films exhibit unconventional resistivity scaling, reaching a room-temperature resistivity as low as 34 μΩ·cm at a thickness of 1.5 nm. [4]

In this work, we demonstrate ultrathin NbP films deposited below 5 nm using atomic layer deposition (ALD) as a scalable and integration-friendly approach. Unlike standard ALD steps, we introduce an additional in-cycle chemical purge step to actively modulate the surface chemistry during film deposition, thereby establishing ALD process for ultrathin NbP. Compared to conventional metals, ultrathin NbP films exhibit favorable electrical transport characteristics with suppressed resistivity degradation upon thickness scaling. Resistivity values remain stable in the sub-5-nm regime, with NbP films exhibiting a resistivity of approximately 300 μΩ·cm, despite seedless deposition on 6-inch wafers at a low temperature of 170 °C. Post-deposition annealing further enhances structural ordering and improves electrical performance. Notably, these thickness-dependent transport characteristics persist even when NbP is deposited on amorphous Si substrates, indicating that the observed behavior is not reliant on epitaxial or crystalline templates.

Despite these advantages, ultrathin NbP films are highly susceptible to oxidation, which poses a critical challenge for reliable electrical characterization and practical integration. To mitigate surface oxidation, capping layers were introduced; however, this approach revealed an additional limitation in the form of interfacial interdiffusion between NbP and the capping layer. These results highlight both the promise of ultrathin NbP as a scalable interconnect material and the importance of interface engineering to fully realize its potential in nanoscale devices.

Acknowledgments: This work was supported by the National Research Foundation of Korea(NRF) grant funded by the Korea government(MSIT)(RS-2024-00357895).

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2:30pm **ALDALE-MoA-5 Metal-polar AlN and GaN Atomic Layer Etching using SF_6 and Cl_2/BCl_3 Plasma**, ***Rafael Panagiotopoulos,*** Cornell University*; Michael Collings, Steven M. George,* University of Colorado at Boulder*; Jeremy Clark, Debdeep Jena, Huili Grace Xing,* Cornell University

State-of-the-art electronic and photonic devices rely heavily on the III-V semiconductors and specifically GaN and AlN. Their properties such as wide bandgaps and inherent polarity make them great candidates for several applications from high electron mobility transistors to ultraviolet emitters and photonic integrated circuits. The above demand increased control and complexity, thus more advanced processing techniques are required. This need for more precise and controllable etching makes atomic layer etching (ALE) a useful pathway in modern devices.

ALE is based on decoupling the etching process into multiple self-limiting steps, thus achieving superior control and minimizing damaged layer extending below the surface associated with conventional reactive ion etching. In this work we report the successful ALE of highly crystalline AlN and GaN utilizing sequential exposures to SF_6 and Cl_2/BCl_3 plasma. This approach yields very high synergy and surface morphology preservation at temperatures as low as 50°C.

Experiments were performed on single-crystalline AlN and GaN films grown on sapphire substrates and film thickness was monitored in real time with in-situ ellipsometry. Each ALE cycle consists of sequential SF_6 and Cl_2/BCl_3 steps separated by Ar purging. RIE power is set to 0 during all steps to maximize chemical interactions and minimize physical etching. Etch rates were found to be 4.47±0.01 Å/cycle and 5.92±0.03 Å/cycle for AlN and GaN. By changing the duration of the removal step, the ALE cycle was found to be self-limiting for both materials (Fig. 1). Each half-reaction was performed separately on clean samples to study the amount of unintended etching. The SF_6 step was found not to etch AlN and GaN, while the Cl_2/BCl_3 step etched AlN and GaN at 0.11±0.02 Å/cycle and 0.14±0.06 Å/cycle respectively. The above lead to ALE synergy values of 97.54±0.45% for AlN and 97.62±1.02% for GaN (Fig. 2). The effects of ICP power during the removal step and temperature were also studied. Increasing ICP power leads to three distinct regions. An ALE window is achieved and higher power leads to spontaneous etching of the materials (Fig. 3). Etch rates were found to weakly depend on temperature all the way down to the boiling point of the chlorides indicating that formation of the chloride is achieved through ion energy, but volatilization is achieved through thermal energy (Fig. 4).

The sample surface was characterized by AFM. Analysis showed a reduction in surface RMS roughness that corresponded to 21.3% for AlN and 30.2% for GaN after 30 cycles of ALE. At the same time, surface morphology is maintained as atomic steps remain defined (Fig. 5). XPS analysis was also used to characterize the mechanism of etching. Scans after exposure to SF_6 plasma show the emergence of a fluoride peak that is effectively removed after exposure to Cl_2/BCl_3 plasma, indicating a mechanism similar to fluorination and ligand exchange in thermal ALE is present (Fig. 6).

2:45pm **ALDALE-MoA-6 Thermal Atomic Layer Etching of Magnesium Oxide Using Hydrochloric Acid and Acetylacetone or Tetramethylethylenediamine**, ***Erin Jacoski***, *Aziz Abdulagatov, Troy Colleran, Steven George,* University of Colorado Boulder

The thermal atomic layer etching (ALE) of magnesium oxide (MgO) was accomplished using sequential exposures of hydrochloric acid (HCl) and acetylacetone (Hacac). The ALE process was further improved using sequential exposures of HCl and tetramethylethylenediamine (TMEDA). MgO ALE is important because MgO is used as a tunneling barrier for magnetic tunneling junctions in magnetoresistive random access memory (MRAM) and spin-transfer torque MRAM devices. Precise control of the tunneling barrier thickness allows for optimization of device performance.

The initial MgO film was grown by atomic layer deposition (ALD) using sequential exposures of bis(cyclopentadienyl) magnesium and water. The deposition and etching were monitored using quartz crystal microbalance (QCM) measurements. The QCM measurements monitored etching by HCl/Hacac at temperatures from 180°C to 240°C. The sequential HCl and Hacac exposures resulted in a linear decrease of MgO film mass versus number of ALE cycles (**Figure 1a**). The etch rates were 0.28 Å/cycle at 180°C and increased to 0.56 Å/cycle at 220°C. The volatile etch products were also identified using quadrupole mass spectrometry (QMS). The QMS results revealed that HCl chlorinates MgO according to MgO + 2HCl ® $MgCl_2$ + H_2O. Then Hacac reacts with $MgCl_2$ to produce volatile $Mg(acac)_2$ species according to $MgCl_2$ + Hacac ® $Mg(acac)_2$ + 2HCl (**Figure 1b**).

The HCl etch product resulting from the Hacac reaction can lead to rechlorination of the underlying MgO surface. To avoid this rechlorination, TMEDA can replace Hacac. TMEDA can react by ligand addition to $MgCl_2$. There is no accompanying hydrogen transfer that can produce HCl. The mechanism during MgO ALE with sequential HCl and TMEDA exposures was confirmed with QMS. HCl again chlorinates MgO according to MgO + 2HCl® $MgCl_2$ + H_2O. Then TMEDA reacts with $MgCl_2$ to produce volatile $MgCl_2$(TMEDA) species by ligand addition according to $MgCl_2$ + TMEDA ® $MgCl_2$(TMEDA) (**Figure 2b**). QCM measurements monitored MgO etching by HCl/TMEDA at temperatures ranging from 200°C to 290°C. The sequential HCl and TMEDA exposures again resulted in a linear decrease of film mass versus number of ALE cycles (**Figure 2a**). The largest MgO etch rate was 1.46 Å/cycle at 270°C.

Atomic Layer Etching
Room Tampa Bay Salons 3-4 - Session ALE-MoA
Plasma and/Energy-Enhanced ALE I

Moderators: Heeyeop Chae, Sungkyunkwan University (SKKU), **Keren J. Kanarik**, Lam Research

4:00pm **ALE-MoA-11 Atomic Layer Processing of Electronic Devices**, ***Andreas Fischer***, *Thorsten Lill,* Clarycon Nanotechnology Research, Inc.*; Fred Roozeboom,* University of Twente, Netherlands **INVITED**

Atomic Layer Etching (ALE) is increasingly adopted to meet atomic-scale patterning requirements in advanced semiconductor manufacturing. This

work presents a comprehensive technical analysis of ALE fundamentals, process mechanisms, and performance metrics with emphasis on processing outcomes relevant to nanoscale and 3D device integration. ALE utilizes sequential, self-limiting surface reactions to achieve controlled etch-per-cycle behavior, enabling sub-nanometer material removal, excellent across-wafer uniformity, and reduced aspect-ratio dependent etching compared to reactive ion etching (RIE). Thermal and plasma-assisted ALE regimes are evaluated with respect to etch selectivity, damage mechanisms, and directionality. Thermal ALE demonstrates highly selective isotropic etching driven purely by surface chemistry, achieving minimal plasma-induced damage and enabling precise removal of oxides and high-k materials critical for advanced gate stacks and 3D architectures. Plasma-assisted ALE enables tunable anisotropy through low-energy ion activation while maintaining atomic-scale precision and improved surface smoothness relative to conventional plasma etching, supporting applications including contact hole formation, sidewall damage removal, and nanoscale pattern transfer. Process comparisons highlight ALE's superior uniformity, reduced excess-energy damage, and enhanced selectivity driven by self-limiting surface chemistry and controlled ion energies. Performance trade-offs—including throughput, precursor safety, chamber contamination, and temperature control—are analyzed to assess scalability toward high-volume manufacturing. The results demonstrate that ALE provides a robust pathway toward atomic-level etch control required for next-generation transistors, stacked memory devices, and heterogeneous material integration. Continued advances in precursor design, plasma control, and process optimization are expected to further expand ALE deployment in future semiconductor nodes.

4:30pm **ALE-MoA-13 Plasma-Enhanced Atomic Layer Etching of Mbe- and Ald-Grown Ultrathin HZO for Ferroelectric Tunnel Junctions***, **Marimuthu Rajendiran**, Nikolai Andrianov, Venkata Raveendra Nallagatla, Joaquín Miranda,* Silicon Austria Labs GmbH, Austria*; Polychronis Tsipas, Stavros Kitsios,* Institute of Nanoscience and Nanotechnology, National Center for Scientific Research "Demokritos", Greece*; Nathan Savoiad, Alexander Flasbyd,* Integrated Systems Laboratory, D-ITET, ETH Zurich, Switzerland*; Athanasios Dimoulas,* Institute of Nanoscience and Nanotechnology, National Center for Scientific Research "Demokritos", Greece*; Laura Bégon Loursd,* Integrated Systems Laboratory, D-ITET, ETH Zurich, Switzerland*; Deluca Marco,* Silicon Austria Labs GmbH, Austria

Abstract

Ferroelectric tunnel junctions (FTJs) based on $Hf_{0.5}Zr_{0.5}O_2$ (HZO) are promising candidates for next-generation non-volatile memory and neuromorphic computing owing to their CMOS compatibility, low power consumption, and fast switching speed. Scaling HZO to ultrathin dimensions (<4 nm) is critical to enhance FTJ performance in neuromorphic computing while maintaining robust ferroelectricity and energy efficiency. In this work, we present a systematic investigation of plasma-enhanced atomic layer etching (PE-ALE) of HZO thin films grown by molecular beam epitaxy (MBE), or by plasma-enhance atomic layer deposition (PEALD). The PEALE process employs a Cl_2/BCl_3/Ar plasma chemistry at a substrate temperature of 50 °C, targeting controlled, layer-by-layer material removal. To support process development, density functional theory (DFT) and molecular dynamics (MD) simulations are used to establish a macroscopic fluid-dynamics-based framework for atomic layer etching, enabling identification of the energy window favorable for monolayer-scale removal of HZO. By tuning key process parameters such as RF power, plasma exposure time, and gas composition, an ALE window for HZO is identified. Furthermore, a comparative study between MBE- and ALD-grown HZO films highlights differences in etching behavior, including process window, surface morphology evolution, and implications for achieving ultrathin ferroelectric layers. These results provide important insights into thickness scaling strategies for ferroelectric HZO and offer a pathway to improve the FTJs device performance.

Reference

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4:45pm **ALE-MoA-14 Atomic Layer Etch Process for Nb and Ta Using CF_4/H_2 Plasma***, **Ryan Walsh**,* University of Nevada, Reno

Atomic layer etch (ALE) processes were developed for Nb and Ta on Si using a CF_4/H_2 plasma for the surface modification step and Ar^+ irradiation for the removal step. These materials are widely used in superconducting quantum device fabrication. The processes were investigated with respect to RF bias, CF_4/H_2 dose time, and Ar^+ etch time in order to identify the ALE window and saturation points. Ta and Nb yielded identical 0.23 +/- 0.01 nm/cycle etch rates for a soft-saturation process. The total cycle time was 16 sec with synergies of > 99% and 87% for Ta and Nb, respectively, and surface roughnesses were significantly reduced as compared to both the as-deposited films and an RIE process with similar chemistry. Over-saturated and under-saturated process were also investigated. A significant difference in EPC between different phases of Tantalum was also observed, suggesting crystal structure plays an important role in etch dynamics. Tantalum Nitride was also investigated due to its thin native oxide, which could help improve superconducting device performance.

To demonstrate the usability of these processes in industry, the effect of reduced purge times on ALE process performance was studied. For all processes the etch per cycle, selectivity, synergy, and surface roughness before and after were reported. A full process for Si was not studied but relevant parameters were reported. These processes are promising for real world manufacturing of devices that are sensitive to damage and require precise etch control.

5:00pm **ALE-MoA-15 Uncovering Plasma-Enhanced Atomic Layer Etching of Silicon Nitride Using Molecular Dynamics Simulations with Machine Learning Force Fields***, **Sungwon Park**, Gyeong Hwang,* University of Texas at Austin

Plasma-enhanced atomic layer etching (PEALE) enables anisotropic etching with atomic-scale precision and low roughness, yet its detailed mechanism remains unclear. Here, we present a molecular dynamics framework with machine-learning force field (MLFF) to study SiN_x PEALE driven by sequential CF_4 adsorption and Ar^+ bombardment. Multi-cycle simulations capture the evolution of the chemically modified layer and reveal descriptors that govern etch behavior.

At low Ar energy (30 eV), the modified layer gradually evolves toward a pseudo-steady state in composition and thickness. Fluorine accumulation saturates at F/Si ≈ 1.0, while carbon remains at consistently low levels due to preferential removal as volatile C–N-containing species (e.g., NCF). Silicon desorbs mainly as SiF_x (SiF_4 dominant with substantial SiF_2), and nitrogen is removed primarily as N_2. The per-cycle N/Si removal ratio converges to ~1.3, indicating that near-stoichiometric SiN_x etching is obtained.

At higher Ar energies (50–70 eV), however, deeper fluorine penetration combined with increased nitrogen sputtering produces an under-coordinated, Si-rich surface. CF_4-derived carbon readily binds to the surface, forming a rigid SiC network within the modified layer. This suppresses SiF_x formation and increases surface roughness, ultimately leading to etch stop.

These results reveal an Ar–energy–dependent transition in carbon fate—from volatile removal to SiC formation—that determines whether SiN_x remains in a steady-etch regime or reaches etch stop. Building on this mechanistic picture, we will also discuss practical strategies to suppress SiC buildup.

5:15pm **ALE-MoA-16 Comparative Study on Atomic Layer Etching Characteristics of Conventional C_4F_8 and Low-GWP C_3F_6***, **Dong Ki Lee**, Chul-Hee Cho, Inho Seong, Dayeon Kang, Shinjae You,* Chungnam National University, Department of Physics, Republic of Korea

Atomic Layer Etching (ALE) has emerged as a critical technology for achieving atomic-scale precision in next-generation semiconductor fabrication. However, the high Global Warming Potential (GWP) of conventional perfluorocarbon gases widely used in the process, such as C_4F_8, necessitates the urgent development of eco-friendly alternative processes. In this study, we investigate the ALE characteristics of C_3F_6, a promising low-GWP candidate, in comparison with conventional C_4F_8 on silicon oxide (SiO_2) and silicon nitride (Si_3N_4) films to evaluate its feasibility for sustainable manufacturing, targeting high-selectivity applications such as the Self-Aligned Contact (SAC) process. The etching process was performed in an Inductively Coupled Plasma (ICP) reactor, where key

parameters including bias power and step times were varied to verify the self-limiting behavior essential for ALE. We primarily focused on analyzing the process windows, etch rates, and etch selectivity derived from both C_4F_8 and C_3F_6 plasmas. Furthermore, to elucidate the reaction mechanisms and difference in dissociation pathways between the two gas systems, Residual Gas Analysis (RGA) was employed to analyze the gas-phase chemistry and monitor the evolution of neutral species and reaction by-products. In this presentation, we will discuss the potential of C_3F_6 to replace C_4F_8 by presenting the comparative analysis of process feasibility and investigating the correlation between plasma species and etch characteristics, thereby providing guidelines for eco-friendly semiconductor processing.

Emerging Materials and Processes
Room Tampa Bay Salons 1-2 - Session EM-MoA

ALD Supercycle Processes

Moderators: Ageeth Bol, University of Michigan, Ann Arbor, **Venkateswara Pallem**, AirLiquide

4:00pm **EM-MoA-11 From Inverse Design to Thin-Film Growth: AI-Guided Discovery of ALD Dielectrics***, **Ngoc Le Trinh**, Wonjoong Kim, Bonwook Gu, Minhyeok Lee, Dohyun Kim, Han-Bo-Ram Lee,* Incheon National University, Republic of Korea

As atomic layer deposition (ALD) is increasingly applied to complex multicomponent materials, selecting viable compositions and phase windows still relies largely on empirical trial and error. This limitation is particularly acute for emerging dielectric materials, where small compositional changes can strongly affect phase stability and electrical performance. To address this challenge, we present an inverse design framework that integrates a generative diffusion model with a line graph neural network (LGNN) to accelerate materials discovery prior to synthesis. The framework is applied to $La_xTa_yO_z$ ternary oxides, a composition space well represented in the Materials Project database and promising for high-k dielectric and wide-bandgap applications, yet experimentally underexplored. The model directly generates candidate stoichiometries together with predicted structural and electronic properties from a learned generative manifold. Selected compositions and prototype structures were experimentally realized using atomic layer modulation (ALM), enabling atomic-scale compositional control. The resulting $La_xTa_yO_z$ thin films crystallize in the predicted orthorhombic phase, and their electrical properties follow trends consistent with model predictions. These results demonstrate an end-to-end pathway from AI-driven inverse design to thin-film synthesis and device-level validation. More broadly, this framework offers a general strategy to reduce trial-and-error in thin-film fabrication by guiding experiments toward the most promising composition and phase regions.

4:15pm **EM-MoA-12 Spatial ALD of Zinc Tin Oxide by Co-Dosing and Supercycles: The Role of Persistent Ligands***, **Poorani Gnanasambandan**,* Eindhoven University of Technology, The Netherlands*; Melika Motaghian,* Spark Nano, Netherlands*; Mariadriana Creatore, Bart Macco,* Eindhoven University of Technology, The Netherlands

Zinc tin oxide (ZTO) has emerged as a versatile material platform with applications spanning thin film transistors [1] and tandem solar cells [2]. Synthesis of ZTO by conventional temporal atomic layer deposition (ALD) using diethylzinc (DEZ) and tetrakis(dimethyamino)tin(IV) (TDMASn) as precursors has been extensively studied following the supercycle approach, wherein a non-linear growth of ZTO is observed. This stems from persistent ligands - already present in the binary processes - which are strongly enhanced when combined in the supercycle. Specifically, the removal of ethyl (Et) ligands from DEZ is much less effective on SnO_2 surfaces [1,3].

Despite offering transformative advantages in processing speed, low thermal budget, and manufacturing scalability, spatial atomic layer deposition (SALD) of ZTO remains largely unexplored. In this work, we investigate the synthesis of $Zn_{1-x}Sn_xO$ films by SALD using both co-dosing and supercycles, and draw a direct comparison between them. We study ZTO films across composition ranges x = 0.1 to 0.6, and deposition temperature of 100-200 ^oC.

Our findings reveal that while binary SnO_2 and ZnO films deposited by SALD are free of carbon impurities, both supercycle and codosing resulted in ZTO films with a maximum of 5. at% and 3. at% carbon, respectively, while no nitrogen is detected. The presence of carbon and absence of nitrogen suggests the persistent Et ligands rather than the N-containing amine ligands to be (partially) incorporated. In-situ ellipsometry during SALD shows a strong nucleation delay for ZnO when interrupted by a single cycle of SnO_2, in line with more strongly-bound persistent Et ligands on Sn-terminated surfaces similar to reported behaviour in temporal ALD processes [1, 3]. Given that both approaches demonstrate bulk-carbon presence, our current work focuses on compositional analysis across the full Zn:Sn ratio range and in-depth surface characterization to fully elucidate similarities and differences between co-dosing and supercycle SALD of ZTO. Of particular interest is the codosing approach, which yields well-mixed films, hence understanding its growth mechanism and impact on film properties will be systematically investigated.

[1] Hung, HN, et al. "Enhancing electronic properties by suppressing nucleation delay for low-temperature processed atomic-layer-deposited amorphous zinc–tin-oxide thin films." *Ceramics International* 50, no. 9 (2024), p:15085

[2] Heydarian, M, et al. "Indium-Free Recombination Layer for Perovskite-Based Multijunction-Solar-Cells-with Improved Performance Using Sputtered Zinc Tin Oxide." *Small* 21, no. 50 (2025), p: e11646.

[3] Mackus, A, J., et al. "Incomplete elimination of precursor ligands during atomic layer deposition of zinc-oxide, tin-oxide, and zinc-tin-oxide." *The Journal of Chemical Physics* 146, no. 5 (2017), p: 052802.

Acknowledgement: This work is supported by the European Union co-funded PEPPERONI (No. 101084251) project.

4:30pm **EM-MoA-13 Atomic Layer Deposition of Epitaxial Complex Oxides for Neuromorphic and Photonic Applications***, **Henrik Sønsteby**,* University of Oslo, Norway **INVITED**

Atomic layer deposition (ALD) famously offers precise control over thickness, uniformity and in some cases, composition. However, its use for the growth of crystalline and epitaxial complex oxides, particularly at low temperatures, remains limited**.** This invited contribution reports on recent progress in ALD process development for complex oxide ferroelectrics and semiconductors. The focus is on precursor chemistry, binary process compatibility and growth control in multicomponent systems relevant for neuromorphic and photonic devices. Together, these developments position ALD not only as a tool for dimensional control, but as a chemically tunable platform for engineering functional oxides beyond conventional process limits.

The work centers on water-free, ozone-based ALD processes for ternary oxides, where reliable control of the binary end members is essential. For $Hf_{0.5}Zr_{0.5}O_2$, low growth-per-cycle processes for HfO_2 and ZrO_2 have been established within overlapping temperature windows. These processes show linear growth behavior, good uniformity, and percent-level control of cation composition through supercycle design. They enable the formation of ferroelectric HZO in very thin films, which is particularly relevant for scaled ferroelectric devices used in neuromorphic computing.

In parallel, new barium precursor chemistries have been developed to address long-standing challenges associated with ALD of Ba-containing oxides. These precursors enable controlled deposition of Ba-containing binary phases using ozone-driven ALD processes at low temperatures. When combined with matching TiO_2 and SnO_2 processes, this approach allows systematic investigation of ternary oxide growth, where stoichiometry, sub-cycle arrangement, and thermal budget can be independently adjusted. Such control is required for $BaTiO_3$- and $BaSnO_3$-based material systems relevant for electrooptic and oxide electronic applications. As an additional outcome, ozone-based ALD of TiO_2 has been demonstrated down to room temperature, providing further flexibility for low-thermal-budget process integration.

Overall, the results illustrate how chemically informed ALD process design can be used to approach crystalline and epitaxial complex oxides under CMOS-compatible conditions. Outstanding challenges related to defect control, crystallization pathways, and transfer to larger substrates are discussed in the context of future device integration. In this context, the work outlines a pathway toward integrating functional complex oxides into future electronic and photonic technologies using ALD as a manufacturable deposition approach.

5:00pm **EM-MoA-15 Towards Fast-Growing Metal Phosphate Films with Controlled Stoichiometry Using Plasma-Enhanced ALD**, ***Aditya Chalishazar**, Ruben Blomme, Lowie Henderick,* Ghent University, Belgium*; Sylwia Klejna,* AGH University of Krakow, Poland*; Matthias Minjauw, Arpan Dhara,* Ghent University, Belgium*; Frans Munnik,* Institute of Ion Beam Physics and Materials Research, HZDR, Germany*; Christophe Detavernier, Jolien Dendooven,* Ghent University, Belgium

Metal phosphates are promising materials for battery electrodes and coatings, corrosion protection coatings, electrocatalysts, and ionic conductors. The versatility of these materials arises due to different binding modes for the metal (M), phosphorus (P) and oxygen (O), resulting in unique structures, stoichiometries, and functional properties. However, controlling the stoichiometry of metal phosphate thin-films using ALD is non-trivial [1]. In this work, we developed ALD processes for Al, Zn, Ti and Sn phosphates, systematically comparing three different approaches (Figure 1) in terms of their strengths and limitations regarding growth characteristics and composition control.

The first approach relies on supercycles to introduce the phosphate backbone. Inspired by [2,3], we combined one metal oxide (MO) ALD cycle with n phosphorus oxide (PO) ALD cycles, using trimethylphosphate (TMP) as the P-precursor and O_2 plasma as coreactant in both the MO and PO subcycles. We observed increased P content as the number of PO cycles per supercycle (n) was increased, varying from MOs to meta/pyrophosphates (atomic P fraction (P_i): 0–23 %; Figure 2(a,d)). However, increasing n beyond a point resulted in moderately increased growth per supercycle (GPSC) with nearly unchanged P content. Our findings, corroborated by computations, indicate that these trends are caused by self-inhibited growth of PO during the supercycle. As such, achieving high P content (P_i > 20%) with this approach comes at the cost of impractically long deposition times.

The second approach relies on TMP plasma polymerisation [1]. Using ALD cycles of TMP plasma, O_2 plasma and M precursor pulses, we developed and compared fast-growing processes for highly P-rich Al, Zn, Ti and Sn meta/ultraphosphate films. Saturated film growth was observed for $T_{dep} \geq$ 300 °C, while a CVD component arises at lower temperatures. As a result, the P content decreases with temperature, offering some compositional control. However, while high growth rates are achieved, this approach is limited to compositions in the high P-range (P_i: 22–26 %; Figure 2(b,d)).

To overcome the limitations of the first two approaches, we developed a novel third approach to achieve high growth rates as well as compositional control from meta/ultraphosphates to P-doped MOs (P_i: 30–10 %; Figure 2(c,d)). Using a supercycle of one TMP plasma-based cycle with n MO ALD cycles, we demonstrate wide compositional tuneability for Al, Zn, Ti and Sn phosphates with high GPSCs.

[1]Henderick et al., *Appl. Phys. Rev.*, **9**, 011310 (2022)
[2]Hornsveld et al., *J. Phys. Chem. C*, **124(9)**, 5495 (2020)
[3]Di Palma et al., *J. Vac. Sci. Technol. A*, **38**, 022416 (2020)

5:15pm **EM-MoA-16 Uncovering Emergent Electrical Behaviour in ALD Nanolaminates Through Supercycle Engineering for SiC Gate Applications**, ***Jesse Kalliomäki**, Soumen Mazumder, Fernanda Albrechtvechietti, Mustafa Yildirim, Safdar Muhammad,* Applied Materials, Finland

Power electronics based on Silicon Carbide (SiC) are central to the green energy transition, enabling high–efficiency electric vehicle (EV) charging and supporting modern power–grid infrastructure. SiC devices are well suited for this task due to their high thermal stability, low ON-resistance ($R_{s,ON}$), and compatibility with existing semiconductor manufacturing. However, optimal performance requires gate-oxides able to withstand high electric fields without excessive leakage or degradation. Traditional thermally grown SiO_2, which were already at a disadvantage due upcoming high aspect ratio device architectures[1], suffers from high interface trap densities at the SiC/SiO_2 interface, limiting device performance[2]. Consequently, improved dielectric materials are needed to meet increasingly demanding application requirements.

This work presents a gate–oxide solution based on nanolaminate metal oxide stacks deposited by Atomic Layer Deposition (ALD). The nanolaminate structure enables record–high breakdown fields (EBD) combined with low leakage and high dielectric constant (k), while adaptive supercycle approach provides precise tunability of material properties to meet device–specific needs. Films were deposited using Applied Materials™ Picosun® ALD systems. With supercycle optimization, high EBD, low leakage, desired flatband voltage (Vfb), high k-value, low interface trap density (Dit) and minimal residual stress are achieved. Electrical properties were evaluated using Hg–probe from samples deposited on Si substrates (Fig 1).

The performance of the nanolaminate stems from precise control of sublayers that disrupt crystallization pathways of the component films. Resulting stratified film stack gives rise to emergent dielectric behaviour through sub–band formation in the periodic structure[3]. Notably, films that tend to crystalize otherwise remains fully amorphous even after annealing, improving electrical reliability.

Process optimization yielded highly uniform films (≈1% or better) with competitive batch–reactor cycle times. Compositional analyses confirm the targeted layer structure and low impurity levels. Electrical characterization demonstrates EBD up to 12 MV/cm, low leakage (<5E-8 @6 MV/cm) and a k-value of ~8, offering higher equivalent oxide thickness and reduced electric–field stress relative to SiO_2. The films also exhibit low Dit values (10^{11} eV^{-1} cm^{-2} range) near the valence band.

These results highlight how advanced supercycle strategies can produce a nanolaminate to rival SiO_2 as the gate dielectric in next–generation SiC MOSFETs.

[1] Micro Nanostruct., Volume 202, 2025, 208126
[2] Energies 2019, 12(12), 2310
[3] Phys. Rev. B 44, 11260

ALD Fundamentals: Growth and Characterization
Room Tampa Bay Salons 5-9 - Session AF-MoP
ALD Fundamentals: Growth and Characterization Poster Session

AF-MoP-1 Novel In/Ga Precursors for Atomic Layer Deposition of IGZO Thin Film Transistors, ***Eunsu Kang***, *Hyunkyung Lee, Ki-yeung Mun, Kyu Hyun Yeom, Hyunkee Kim, Dae Won Ryu,* Hansol Chemical, Republic of Korea*; Jin-Seong Park,* Hanyang University, Korea

Recently, amorphous oxide thin film transistors(TFTs) have been widely studied for applications such as wearable electronics, large scale displays, optical sensors and etc., owing to their promising properties: high mobility, uniformity, and good transmittance.[1]

In this work, we developed non-pyrophoric indium precursor (DMITN) and gallium precursor (DMGTN), which are thermally stable and implemented wide atomic layer deposition (ALD) windows. The physical characteristics were investigated by differential scanning calorimetry (DSC) and thermo-gravimetric analysis (TGA). The non-volatile residues of indium and gallium precursors were about 3.5% and 1%, respectively.

The oxide films (In_2O_3 and Ga_2O_3) were deposited by ALD using O_2 plasma and ozone as oxygen sources. The deposited oxide films were studied via ellipsometer, XPS, XRD, and TEM. In O_2 plasma system, self-limiting growth properties of DMITN and DMGTN were observed 0.9 Å/cycle at 100–250 °C respectively. In particular, the ALD of In_2O_3 film using ozone as an oxygen source was also showed wide ALD window of 250–320 °C and growth rate of 1.0 Å/cycle (Figure 1). In addition, no carbon and nitrogen impurities were detected at all growth temperatures for all films.

The Indium-Gallium-Zinc-Oxide Thin Film Transistors (IGZO TFTs) were fabricated using DMITN, DMGTN, and commercially available for zinc precursor as the n-channel active layer by ALD. The electro-properties of oxide TFTs, compared to oxide TFTs using representative In and Ga precursor, were observed equal or above figures in terms of mobility, threshold voltage, and subthreshold gate voltage swing (Figure 2). The new indium and gallium precursors have demonstrated potential as n-channel active layer materials in oxide semiconductor transistors.

AF-MoP-2 Optimization of Ferroelectric Ga-Doped HfO_2 Thin Films via Peald for Enhanced Phase Stability and Memory Performance, ***Jiseop Byeon***, *Suhyeon Park, Minjae Kwon,* Kyungpook National University, Republic of Korea*; Roy Byung Kyu Chung,* Kyungpook National University

The rapid expansion of Artificial Intelligence (AI) workloads has intensified the demand for high-performance, low-power nonvolatile memory devices. HfO2-based ferroelectrics, particularly Hafnium Zirconium Oxide (HZO), have attracted significant attention due to their excellent CMOS compatibility.[1] However, challenges such as the wake-up effect, limited endurance, and leakage current necessitate further materials and process optimization.To enhance ferroelectric performance, suppressing the non-polar monoclinic phase while promoting the polar orthorhombic (o)-phase is critical. Recent AI-driven and DFT-based screening studies identify Ga as a promising dopant for stabilizing the o-phase.[2] The incorporation of Ga effectively modulates lattice parameters, facilitating phase stabilization through controlled lattice strain. In this study, we deposit o-phase Ga-doped HfO2 (HGO) thin films using plasma-enhanced atomic layer deposition (PEALD) and investigate their phase stability and ferroelectric properties for device applications. Specifically, we report on the impact of Ga/Hf sub-cycle ratio during the PEALD process on the remnant polarization and coercive field.Furthermore, integrating optimized HGO thin films into practical architectures, such as Ferroelectric Field-Effect Transistors (FeFETs) and FeNAND, is expected to enable wide memory windows and improved endurance. Therefore, we conclude by evaluating the performance of HGO/IGZO devices and their compatibility with back-end-of-line processing.Reference[1] Cheema, S.S., Kwon, D., Shanker, N. et al. Enhanced ferroelectricity in ultrathin films grown directly on silicon. Nature 580, 478–482 (2020). [2] Yan, S., Xu, P., Li, G. et al. Artificial intelligence-driven phase stability evaluation and new dopants identification of hafnium oxide-based ferroelectric materials. npj Comput Mater 11, 2 (2025)

AF-MoP-3 $AlPO_4$ and AlP_xO_y by Dual-Source and Supercycle PEALD Approaches, ***Florian Preischel***, Leibniz Institute for Solid State and Materials Research, Germany*; Karl Rönnby, Michael Nolan,* Tyndall National Institute, University College Cork, Ireland*; Harish Parala, Anjana Devi,* Leibniz Institute for Solid State and Materials Research, Germany

Aluminum phosphate ($AlPO_4$) is a dielectric material with high chemical and temperature resistance[1,2] making it suitable for use as a protective coating in lithium-ion batteries[3,4] and for high-temperature applications.[5-7] It features a microporous structure of PO_4 and AlO_4[1] and has been proposed to exist as a stable two-dimensional (2D) bilayer form with inherent, molecular-sized pores and no covalent bonds to its substrate.[8] With such a structure and high stability, bilayer $AlPO_4$ could serve as a selective gas-separation membrane. Atomic layer deposition (ALD) is a powerful technique for depositing thin films with high quality, conformality, and precise thickness control, which are essential for achieving the bilayer structure. Utilizing plasma as the co-reactant in plasma-enhanced ALD (PEALD), enables deposition at lower temperatures and provides an additional parameter to modify and control the material composition. For the deposition of ternary materials by ALD, different strategies are viable.[9] In a previous study, Blomme et al. employed PEALD supercycles of $P(NMe_2)_3$ and TMA, both with O_2 plasma as the co-reactant, demonstrating the applicability of this approach for the deposition of AlP_xO_y with tunable composition.[10] In this study, we compare two approaches: using a dual-source precursor that introduces both Al and P, versus combining two individual ALD cycles into a supercycle.

We have identified trimethylaluminum triisopropylphosphine (TMAPIP) as a promising dual source precursor with favorable thermal properties (**Figure 1a**). However, a PEALD process using TMAPIP and O_2 plasma resulted in AlP_xO_y layers with only a few percent P incorporation (**Figure 1b**), indicating a chemisorption pathway involving the loss of the phosphorous adduct.

In a second approach, in conjunction with density functional theory (DFT) calculations, we developed a supercycle process that combines individual PEALD cycles of trimethylaluminum (TMA) and $P(NMe_2)_3$ from 60 °C to 240 °C (**Figure 2a**). This route enables controlled tuning of the AlP_xO_y composition by varying the deposition temperature and supercycle sequence, as shown by Rutherford backscattering spectrometry (RBS) (**Figure 2b**) and XPS. By combining two $P(NMe_2)_3$ sub-cycles with one TMA sub-cycle, the deposition of stoichiometric $AlPO_4$ is achieved (**Figure 2c**). Using the optimized PEALD process in initial downscaling experiments, we deposited $AlPO_4$ with an approximate thickness of 3 nm in a continuous, homogeneous thin film, as revealed by transmission electron microscopy (TEM) (**Figure 2d**). This finding provides a strong foundation for further exploring the bilayer structure of $AlPO_4$.[11]

AF-MoP-4 Correlative AFM-SEM for ALD Characterisation, ***Satyam Ladva***, Quantum Design inc.

Background. Atomic Layer Deposition (ALD) provides sub-nanometer thickness control and excellent step coverage in 3D device architectures, but ultra-thin films and spatial variability often make single-technique metrology inconclusive.

Approach. We demonstrate a correlative workflow that couples Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM) using Quantum Design's FusionScope AFM-with-SEM platform and the AFSEM®nano AFM insert for Cryo-SEM/FIB systems. SEM is used to rapidly localize thin-film defects (pinholes, particles, seam voids, trench-edge non-uniformity), followed immediately by AFM on the identical region for quantitative height and roughness, plus functional contrast when needed.

Key capabilities. FusionScope enables AFM-SEM-EDS correlation through a shared coordinate system and real-time overlay, minimizing the common "find it again" failure mode in thin-film analysis. Relevant operating ranges include a closed-loop 22 × 22 µm AFM scan with 11 µm Z range and <50 pm imaging noise, alongside a thermal field-emission SEM operated from 3.5–15 kV with pA–nA probe currents under high vacuum. Beyond standard contact/dynamic AFM, advanced modes (e.g., stiffness/adhesion mapping) and interchangeable probes support conductive and magnetic measurements.

In-chamber extension. AFSEM®nano brings closed-loop AFM into existing Cryo-SEM/FIB tools for in situ AFM inside the SEM chamber, with compatibility for nanomanipulators and device biasing. This is particularly valuable on FIB-prepared cross-sections, where sidewall thickness, interfacial roughness, and localized conduction pathways can be mapped at the same coordinates where SEM provides microstructural context.

Outcome. The combined approach shortens the loop between ALD process changes and actionable metrics (step height/thickness, RMS roughness, defect density, stiffness/adhesion contrast, localized conductivity) across planar films and complex 3D semiconductor structures.

Keywords: ALD, correlative microscopy, AFM, SEM, EDS, thin films, failure analysis, 3D semiconductors

AF-MoP-5 A Versatile Low-Temperature Pathway for Epitaxial Integration of Functional Nitrides via Hydrogen-Manipulated Atomic Layer Epitaxy, ***Kuan-Cheng Huang***, *Fong-Jyun Jhong, Yu-Sen Jiang, Miin-Jang Chen,* Department of Materials Science and Engineering, National Taiwan University, Taiwan

High-quality epitaxial growth of nitride thin films remains a critical challenge in conventional low-temperature atomic layer deposition (ALD) due to limited surface kinetics and steric hindrance from precursor ligands. To address this challenge, we introduce a novel strategy referred to as Hydrogen-Manipulated Atomic Layer Epitaxy (HM-ALE), which enables low-temperature epitaxial growth of diverse functional nitride materials at a low temperature of 300 °C by reconfiguring the ALD cycle to precisely control surface reactions at the monolayer scale. For GaN and AlN growth, an H_2 plasma step is introduced prior to N_2 plasma exposure, which mitigates steric hindrance from organic ligands (e.g., methyl groups from TMA or TMG) and enhances adatom mobility and surface reconstruction. This synergistic effect facilitates long-range atomic ordering prior to the reaction with nitrogen species. The ω-2θ XRD patterns demonstrate a pronounced enhancement of the (0002) diffraction signal, while high-resolution TEM images further confirm high-quality epitaxial AlN and GaN films with well-resolved lattice fringes on sapphire substrates. For TiN growth, the HM-ALE method yields low resistivity and high crystalline quality with a well-defined epitaxial relationship and a sharp interface with sapphire substrates as confirmed by high-resolution TEM. Overall, HM-ALE provides a robust low-temperature pathway for epitaxial integration of functional nitrides, ranging from wide-bandgap nitride semiconductors to metallic nitride conductors, and offers new opportunities for nitride-based heterostructures under stringent thermal budget constraints.

AF-MoP-6 Study of the Chemical Stability of Precursors Used for ALD of Lithium-Containing Films by Structural and Thermal Analyses, ***Nicolas Massoni***, *Manon Letiche, Sylvain Poulet,* CEA/LETI-University Grenoble Alpes, France*; Pierre-Alain Bayle,* CEA-University Grenoble Alps, France*; Névine Rochat,* CEA/LETI-University Grenoble Alpes, France*; Rodica Chiriac, François Toche,* Université Claude Bernard Lyon 1, LMI, UMR CNRS 5615, France*; Messaoud Bedjaoui,* CEA/LETI-University Grenoble Alpes, France

Lithium-based batteries are well-known and robust energy storage solutions for portable devices. The widespread electrolyte material employed for microbatteries is a LiPON thin film [1]. It can be deposited by ALD with organic precursors permanently heated into tanks, during several weeks. In this study, the impact of ageing of lithium hexamethyldisilazide (LiHMDS) and diethylphosphoramidate (DEPA) precursors, *i.e.* the time elapsed in their storage tanks, on their chemical stability is reported. It was already shown that LIHMDS was stable and only DEPA chemically degrades after 14 days of ageing [2].

Three DEPA suppliers, designated by the letters A, B and C, were compared, and significant differences were found, before and after ageing. The as-supplied DEPA purity was identical (98%) for all. However, their ^{1}H NMR spectra revealed that B and C shared the same structure, which was different for A. After 30 days of ageing at 90°C in a heated tank, significant differences were observed. For supplier A, the powder has agglomerated and turned in brown, whereas it remained white and flowable for suppliers B and C. As shown by FTIR, the brown aged DEPA has lost most of its NH_2 bonds. And ^{31}P NMR DOSY experiment has confirmed the agglomeration. When LiPON is deposited with the A DEPA, its ionic conductivity progressively drops over ageing time, with an overall loss of one decade between the as-supplied and the most aged precursor. Since the amine group is known to be involved in the conduction mechanism of LiPON, this is a direct consequence of the amine loss. For suppliers B and C aged in the same conditions, they kept their initial color and texture. Moreover, FTIR revealed that the NH_2 group was no impacted at all by ageing. This different ageing behavior may lie in the composition of the as-supplied products (currently investigated by DSC), or in the starting structure as already evidenced by NMR.

Finally, it is expected that LiPON deposited with DEPA from suppliers B or C, will not show any deleterious impact on its ionic conductivity (in progress).

[1] Sallaz et al, 2024, https://doi.org/10.1021/acselectrochem.4c00022

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AF-MoP-7 Deposition and Electrical Characterization of Hafnia ALD Thin Films Using Cp–Based Precursors, ***Hyun Woo Jeong***, CN1 Co.,Ltd, Republic of Korea

HfO_2 thin films were deposited by thermal atomic layer deposition (ALD) using a thermally stable cyclopentadienyl-based hafnium precursor (CpHf) and comparatively evaluated as a function of oxidant chemistry (H_2O vs O_3) for charge-trap memory (CTM) applications. Deposition was carried out on a 300 mm single-wafer ALD system (Atomic Premium, CN1 Co., Ltd.) at 320 °C and 0.45 Torr. GPC and RI were extracted by systematically varying precursor/oxidant pulse and purge times to establish optimized process recipes. For the H_2O process, saturated growth was achieved with CpHf 1 s and H_2O 1 s, and film uniformity significantly enhanced when purge times were increased to 20 s, yielding an average GPC of 0.058 nm/cycle and RI of 2.00. For the O_3 process, growth stability improved with longer O_3 exposure; the optimized recipe (CpHf 1 s / purge 20 s / O_3 5 s / purge 20 s) exhibited a higher average GPC of 0.068 nm/cycle with RI of 1.99. CTM capacitors with a Si/SiO_2 (2 nm)/HfO_2 (10 nm)/Al2O3 (10 nm)/Au stack were fabricated and post-deposition annealed at 350, 400, and 450 °C. X-ray diffraction showed no crystallization of either Al_2O_3 or HfO_2 for all anneal temperatures.

Electrically, O_3-processed devices exhibited larger C-V memory windows than H_2O-processed devices under identical measurement conditions, with the largest difference after 350 °C annealing. Fowler–Nordheim analysis and constant-current stress indicated relatively minor degradation at 350 °C, the H_2O process yielded an overestimated apparent barrier suggesting defect-induced mixed conduction, whereas the O_3 process retained linear FN behavior consistent with dominant FN tunneling. Endurance cycling confirmed stable memory windows of ~6.0–6.2 V over 10^1–10^4 cycles for O_3-based devices, while H_2O-based devices degraded from 0.823 to 0.691 V. Overall, O_3 is a more favorable oxidant for CpHf-based HfO_2 ALD, improving both process efficiency (GPC) and CTM memory characteristics (window and endurance).

AF-MoP-8 Low-Temperature High-Quality Epitaxial Aluminum Nitride Films Deposited by Plasma-Enhanced Atomic Layer Deposition, *Pini Medved,* Ariel University, Ariel 40700, Israel*; Silvia Piperno,* Bar-Ilan University, Ramat Gan 5290002, Israel*;* ***Valentina Korchnoy,*** Technion Israel Institute of Technology, Israel*; Gili Cohen-Taguri,* Bar-Ilan University, Ramat Gan 5290002, Israel*; Asaf Albo,* Ariel University, Ariel 40700, Israel

Aluminum nitride (AlN) is an ultra-wide-bandgap semiconductor (6.2 eV) with applications in optoelectronics and high-power electronics due to its high thermal conductivity, low thermal expansion coefficient and high dielectric strength. Conventional deposition techniques for high-quality AlN, such as metal-organic chemical vapor deposition and molecular beam epitaxy, typically require temperatures exceeding 700 °C, limiting integration with temperature-sensitive materials and pre-existing layers.

In this work, we demonstrate the deposition of single-crystal AlN films on gallium nitride (GaN) templates at a substrate temperature of 300 °C using plasma-enhanced atomic layer deposition (PEALD), without additional energetic plasma exposures or *ex situ* annealing. The deposition was carried out in an Ultratech Fiji G2 PEALD system on *c*-plane GaN-on-sapphire substrates. Prior to growth, the substrates were exposed to a remote N_2–Ar plasma to condition the surface. Each PEALD cycle consisted of a trimethylaluminum (TMA) precursor pulse followed by a remote N_2–Ar plasma co-reactant step under low-pressure conditions optimized for epitaxial growth.

High crystalline quality is evidenced by narrow X-ray diffraction rocking curves of 288 arc sec (0.08°) for 10 nm films and 497 arc sec (0.138°) for 70 nm films. Continuous epitaxial growth across the full film thickness is confirmed by high-resolution transmission electron microscopy and selected-area electron diffraction. Atomic force microscopy reveals smooth surface morphologies with sub-nm roughness.

This research demonstrates a PEALD-based approach for achieving high-quality, single-crystal AlN films at 300 °C, enabling III-nitride integration into low-thermal-budget platforms without additional *in situ* energetic plasma exposure or *ex situ* annealing steps that may degrade film quality.

This presentation discusses the results published in Ref. [1].

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The work is the subject of a pending U.S. patent application (No. 63/844,832).

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AF-MoP-9 ALD of Zinc Phosphate films with Tuneable Structure and Stoichiometry, ***Aditya Chalishazar,*** *Arpan Dhara,* Ghent University, Belgium*; Sylwia Klejna,* AGH University of Krakow, Poland*; Matthias Minjauw,* Ghent University, Belgium*; Eduardo Solano,* ALBA Synchrotron, Spain*; Frans Munnik,* Institute of Ion Beam Physics and Materials Research, HZDR, Germany*; Christophe Detavernier, Jolien Dendooven,* Ghent University, Belgium

Metal (M) phosphates are compatible with diverse applications that span battery technology, corrosion protection, electrocatalysis, and proton conduction. Phosphate polymorphs have multiple structures and stoichiometries, with the P/M ratio profoundly impacting their functional properties and applicability [1]. Atomic layer deposition (ALD) of metal phosphate films commonly combines metal oxide (MO) and phosphorus oxide (PO) cycles in supercycles. Trimethylphosphate (TMP) is the most-used P source for ALD, combined with H_2O, O_3 or O_2 plasma as oxidants [1-3].

In this work, we first investigated the ALD growth of PO using alternating TMP and O_2 plasma exposures. *In-situ* spectroscopic ellipsometry (iSE) and *in-situ* reflection Fourier transformed infrared (FTIR) spectroscopy revealed self-inhibited growth – an initially high growth on oxide surfaces, followed by rapid saturation with continuing film growth (Figure 1(a)).

Next, we developed a new plasma-enhanced ALD supercycle to grow zinc phosphate (ZnPO) films by combining one ALD cycle each of ZnO (DEZ/O_2 plasma) and PO (TMP/O_2 plasma) at 150 °C. The process demonstrated self-limiting film growth and resulted in the deposition of P-doped ZnO films, with improved (compared to [4]) but limited P incorporation of ca. 11 at.% (Figure 1(b)).

Increasing the number of PO cycles (n) from 1 to 5 in the [1·(ZnO) – n·(PO)] supercycle improved the P incorporation in the films, whose composition varied from P-doped ZnO to zinc metaphosphate ($ZnPO_3$) (Figure 2(a)). Our data also suggested that the PO interlayers impact the long-range order of ZnO layers within the as-deposited films, impacting their crystallinity (Figure 3(g)). However, we observed concurrent reduction in both the growth per supercycle (GPSC) as well as elemental Zn and P incorporation for the films for $n \geq 3$ (Figure 2(b,c)).

Experimental and computational data elucidated the dependence of film growth on the composition of the growth surface. ZnO growth is suppressed on a PO surface, resulting in self-inhibited film growth for the supercycle. This self-inhibited growth, in combination with nucleation effects for ZnO ALD on PO surfaces, results in the deposition of increasingly rough films, as n increases (Figure 3(a–f)). Overall, this work highlights the need to consider the interactions between the precursors and growth surfaces during the development of similar ALD supercycles for other metal phosphate families.

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AF-MoP-10 Non–Magnetizing Microwave PEALD Enabled via Magnetic Shielding for Highly Uniform Double-Sided Al_2O_3 Film Deposition, *Michel Marti,* ***Alejandra Vanessa,*** *Ramis Hertwig, Dominik Hartmann,* Evatec AG, Switzerland

Plasma enhanced atomic layer deposition (PEALD) is a key technique for the low temperature fabrication of conformal, high quality thin films used in semiconductor, photonic, and MEMS technologies. In microwave driven PEALD systems, magnetic fields are commonly employed to stabilize the plasma and tailor electron density. However, these fields may unintentionally magnetize magnetic or magnetically sensitive substrates, limiting the applicability of the process for advanced device architectures [1,2]. Recent reviews of ALD process engineering have emphasized the importance of reactor design, plasma configuration, and substrate specific constraints, including magnetic sensitivity, when targeting precision thin film properties in industrial ALD platforms [3].

In this work, a non-magnetizing microwave PEALD approach for Al_2O_3 thin films is demonstrated in a batch processing tool enabling simultaneous double-side wafer deposition with excellent conformality and coverage on both sides. A dedicated magnetic shielding concept was developed specifically for this batch architecture, where magnetic neutrality and highly uniform film properties across both wafer surfaces are critical. Three-dimensional magnetic field simulations were used to guide the design of a magnetic absorber, systematically evaluating the influence of shield size, aperture geometry, and distance to the substrate on the magnetic flux density at the sample position. The finalized shielding concept was implemented directly into the PEALD reactor without compromising plasma ignition or stability.

Magnetic field measurements confirmed that the shielding reduced the magnetic field at the substrate position below the magnetization threshold of sensitive materials, preventing permanent substrate magnetization during plasma exposure. Subsequently deposited films exhibited excellent thickness uniformity on each side of each substrate, stable refractive index, and strong wafer to wafer reproducibility.These results establish a viable route for non-magnetic PEALD processing in microwave plasma environments and provide a framework for integrating magnetic field mitigation strategies into industrial ALD systems for sensitive applications.

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AF-MoP-11 Amine Adducts of Cyclopentadienyl Magnesium as Precursors for Magnesium Containing Films Deposition, ***Anuththara Arachchige,*** *Hima Kumar Lingam, David Roberts,* Ereztech Labs LLC

Magnesium–containing thin films—including magnesium oxides, magnesium fluoride, magnesium nitrides, and magnesium–doped GaN/ZnO—are useful for energy storage, electrical insulation, and optical coatings. Cyclopentadienyl–magnesium precursors ($Mg(RCp)_2$) are widely used in deposition studies because they are highly volatile, thermally stable, and strongly reactive toward co–reagents. However, most of these manganocene compounds are pyrophoric, making them difficult to store and handle. The present study describes the synthesis of magnesium cyclopentadienyl amine adducts, which mitigate the pyrophoricity of the parent compounds while maintaining desirable precursor characteristics.

Here, we describe the synthesis of amine adduct of magnesium cyclopentadienyl complexes, Mg(MeCp)2TMEDA (1), Mg(MeCp)2TEEDA (2), Mg(MeCp)2TMPDA (3), Mg(MeCp)2TMBDA (4), Mg(EtCp)2TMEDA (5), Mg(MeCp)2TEEDA (6) (Fig. 1). Pure complexes 1-6 were obtained by sublimation at low vacuum. Purity and structures were confirmed by 1H NMR, 13C NMR, and X-ray crystallography. Thermal behavior and volatility of complexes was investigated by TG and DSC. Compound 1-6 showed clear evaporation with <0.5% residue after 200° C (Fig 2). Preliminary air-exposure testing indicated that none of the compounds exhibit spontaneous ignition when exposed to air. Overall, complexes 1–6 exhibit promising properties as precursors for magnesium–containing metal depositions, and their reduced pyrophoricity relative to the parent compounds offers clear advantages for safer storage, transfer, and handling.

Lingam, H. K.; Arachchige, A. A.; Roberts, D. A. Amine adduct of group 2 metallocene precursors for deposition of group 2 metal films for Ereztech Labs. US. Pat. Appl. US 2025/0353865 A1, 2025.

AF-MoP-12 Kinetics of the Atomic Layer Deposition Trimethyl Aluminum – Ozone Reaction Studied Through Variations of Surface Area and Temperature with *in-Situ* Quadrupole Mass Spectrometry, ***Eric Bissell,*** *Jacob Furst,* University of Central Florida*; Nicholas G. Rudawski,* University of Florida, Gainesville*; Fernando Uribe-Romo, Titel Jurca, Kathleen Richardson, Parag Banerjee,* University of Central Florida

Ozone (O_3) is investigated as a co-reactant with trimethylaluminum (TMA) for atomic layer deposition (ALD) of Al_2O_3 on ZnOnanopowders, producing core-shell powders subsequently densified into ceramics. O_3 is explored as an alternative to H_2O due to the propensity of moisture to form capillary bridges in nanoparticle beds, leading to strong interparticle cohesion, reactant retention, and non-ideal ALD behavior including parasitic chemical vapor deposition-like growth and powder agglomeration.1Minimizing agglomeration is critical because the Al_2O_3 coating is intended to act as a

diffusion barrier that suppresses ZnOgrain growth during sintering for nanocrystalline ceramic fabrication.

Nanoparticle beds exhibit high specific surface areas (18 m^2 g^{-1} in this study), resulting in ALD processes that are transport-limited within the powder bed. Consequently, extended exposure and purge times are often required for half-reactions to approach saturation, presenting challenges for scalable powder coating.

In this work, the effects of reactor temperature and powder mass loading on O_3-based ALD kinetics are examined using a rotary powder ALD reactor. ZnO nanoparticle loadings of 0 g (empty reactor), 1 g (18 m2), 3 g (54 m2), and 6 g (18 m2) are studied at temperatures of 120 °C, 175 °C, and 250 °C. Reaction progress is monitored in situ using a quadrupole mass spectrometer (QMS) residual gas analyzer (RGA) to track gas-phase reactant consumption and reaction by-products during each half-cycle. Powder surface area before and after coating is measured using the Brunauer–Emmett–Teller (BET) method.

Across all temperatures and powder loadings examined, QMS-RGA signatures associated with the TMA half-reaction exhibit progressively shorter saturation times with increasing ALD cycle number. BET measurements indicate no appreciable change in total surface area following coating. Taken together, these observations suggest a progressive reduction in the density or accessibility of reactive surface sites during cycling, consistent with incomplete surface regeneration during the O_3 half-reaction under the conditions studied. These effects are attributed to transport limitations and/or rapid recombination of ozone-derived oxygen species within the nanoparticle bed, which may hinder full restoration of reactive sites between cycles.

This work demonstrates that while O_3 effectively mitigates moisture-induced agglomeration in nanoparticle ALD, its transport and reaction characteristics can limit surface renewal in highsurfacearea powder systems, thereby constraining its effectiveness as an oxidant for conformal coating of dense nanoparticle beds.

AF-MoP-13 Phase-engineered TiO_2–RuO_2 top interface for a High-k TiO_2 dielectric with bottom interfacial stabilization via a ZrO_2 layer in Tin-based DRAM capacitors, ***Kyungmo Yang***, *Woojin Jeon, Chaeyeong Hwang,* Kyung Hee University, Republic of Korea

As DRAM devices continue to scale down, dielectric materials that can simultaneously provide a high dielectric constant and low leakage current are required to secure sufficient capacitance within a reduced cell area. In metal–insulator–metal (MIM) capacitor structures employing TiN bottom electrodes, oxygen scavenging by TiN induces interfacial degradation, leading to increased oxygen vacancy formation in adjacent oxide dielectrics and consequent degradation of electrical reliability. Although TiO_2 has been widely investigated as a high-k dielectric candidate, its relatively small band gap and unstable interface with TiN limit its applicability in single-layer configurations.

In this study, a ZrO_2/TiO_2 stacked dielectric structure incorporating a ZrO_2 buffer layer between the TiN bottom electrode and the TiO_2 dielectric is proposed to alleviate interfacial degradation and suppress leakage current. Electrical characterization revealed that TiO_2 single-layer capacitors exhibited pronounced DC nonlinearity and increased leakage current due to poor interfacial properties at the TiN/TiO_2 interface. In contrast, the introduction of a ZrO_2 buffer layer significantly reduced dielectric loss and leakage current, resulting in improved capacitance stability. Chemical analysis confirmed that the ZrO_2 buffer layer effectively suppressed oxygen scavenging from the TiN electrode, thereby reducing oxygen vacancy formation in the TiO_2 layer and enhancing interfacial stability.

Furthermore, recrystallization induced by the oxide top electrode was utilized to enhance the dielectric constant. When sufficient thickness was provided, the ZrO_2 and TiO_2 films were well crystallized into tetragonal-ZrO_2 and anatase-TiO_2 phases, respectively. As the TiO_2 thickness decreased, a localized phase transformation from anatase to rutile TiO_2 was induced at the interface with the oxide top electrode, contributing to an enhanced dielectric constant. Systematic variation of the ZrO_2/TiO_2 thickness ratio revealed a trade-off between dielectric constant and leakage current, with thicker ZrO_2 layers providing superior leakage suppression. In particular, a ZrO_2 buffer thickness of 7 nm or greater was found to be effective in achieving low leakage characteristics while maintaining an enhanced dielectric response.

These results demonstrate that the ZrO_2/TiO_2 stacked dielectric architecture, in which TiO_2 thickness is controlled to realize mixed anatase–rutile phases, is a promising dielectric design for next-generation TiN-based DRAM capacitor applications.

AF-MoP-14 Influence of Process Pressure on the Growth Kinetics and Electrical Properties of NbN Thin Films Prepared by PEALD using TBTDEN, ***Hae Yong Jeong***, *Shin Keun Kim, Taek Kim,* Korea Advanced Nano-fab Center, Republic of Korea

Niobium nitride (NbN) is a pivotal material for superconducting electronics and advanced barrier layers due to its excellent thermal and chemical stability. Among various deposition methods, Plasma-Enhanced Atomic Layer Deposition (PEALD) provides the advantage of high-quality film growth at relatively low temperatures with precise thickness control. In this study, we investigated the influence of process pressure, precisely controlled via pumping valve modulation, on the growth kinetics and material properties of NbN films. The films were synthesized using tert-butylimido-tris-diethylamido-niobium (TBTDEN) as the Nb precursor and N2/H2 plasma as the reactant. The deposition was conducted at a substrate temperature of 350ºC, with the process pressure varied by adjusting the pumping valve position from 18% to 11.5%. Experimental results indicate that variations in process pressure play a decisive role in modulating film characteristics. Specifically, the growth per cycle (GPC) exhibited a measurable response to pressure changes, shifting from 0.927 Å/cycle at an 18% valve opening to 0.872 Å/cycle at 11.5%. This shift suggests that the pressure environment significantly influences precursor residence time and the flux of reactive species, thereby affecting surface reaction efficiency. Furthermore, the electrical resistivity showed a notable improvement with increasing pressure (decreasing valve opening), dropping from 298 μΩ·cm at 18% to 229 μΩ·cm at 11.5%. This trend indicates that higher pressure conditions may promote film densification and optimize stoichiometric nitrogen incorporation. Preliminary structural observations suggest a strong correlation between these electrical improvements and enhanced crystallinity. Detailed X-ray Diffraction (XRD) analysis and X-ray photoelectron spectroscopy(XPS) depth profiling are currently underway to further elucidate the relationship between pressure-driven plasma chemistry and the microstructural evolution of the NbN films. This work demonstrates that process pressure is a critical parameter for tailoring PEALD-NbN properties, providing essential insights for optimizing NbN films in next-generation quantum applications.

AF-MoP-15 Oxide Film Properties Using OH Radicals Generated by Water Vapor Mixed Pure Ozone Gas as ALD Oxidant, ***Naoto Kameda***, MEIDENSHA corp., Japan*; Kenichi Uehara, Shigeo Yasuhara,* Japan Advanced Chemicals Ltd., Japan*; Soichiro Motoda, Tetsuya Nishiguchi,* MEIDEN NANOPROCESS INNOVATIIONS Inc., Japan

The gate dielectric oxide film (e.g. HfO_2) for FET requires low impurity levels and excellent electrical properties. ALD enables the deposition of high-quality gate oxide films, and O_2 plasma, which generates highly reactive atomic oxygen (O radical), has been widely used. However, recent FET devices have become increasingly stacked (e.g., GAA), gate dielectric films must be deposited deep into nanometer-scale microfabricated trenches exceeding an aspect ratio of 100.O_2 plasma ALD cannot deposit the HfO_2 film inside trenches with aspect ratios over 50 due to the deactivation of O radical within trench diffusion[1]. We have reported the high quality of Al_2O_3 film properties by ALD using pure ozone gas (PO-ALD), which is high-concentration pure ozone gas (≥80 vol%) as the oxidizing source and reported the Al_2O_3 film can be formed in trenches with high aspect ratio(> 1500) [2], while cannot deposit with low aspect ratio (<100) using O_2 plasma[1]. Furthermore, it was reported that highly reactive OH radicals can generate by mixing water vapor with high-purity ozone gas at 250ºC[3]. This presentation discusses the effect of using OH radicals as an ALD oxidation source on the film quality of HfO_2 films.

Figure 1 shows the schematic ALD chamber and gas piping systems. The distribution of the gas phase temperature inside the chamber by a hot wall method is controlled to under 100ºC upstream of the substrate, and to substrate temperature (>150ºC) of the downstream the substrate. These temperature distribution is the generation of atomic oxygen near the substrate through the thermal decomposition reaction of ozone ($O_3 \rightarrow O_2+O$).By supplying a mixed gas of ozone and water vapor under these temperature conditions, the ozone thermally decomposes near the substrate, generating O, which then reacts with H_2O to generate OH radicals, which can then be supplied to the substrate (see Fig. 2). Gas supply conditions for ozone and water vapor (flow rate mixture ratio, etc.) are determined by increasing ahing rate at the substrate position due to the supply of OH radicals. Precursor and carrier gases are TDMAH($((CH_3)_2)_4Hf$) and Ar, respectively. Figure 3 shows the relationship between the number

of ALD cycles and HfO_2 film thickness at a substrate temperature of 200°C. The introduction of water vapor slightly increases the film thickness. The estimated GPC are 0.138 nm/cycle(with water vapor) and 0.126 nm/cycle (w/o water vapor), respectively. We will report on film quality, including a comparison of impurity levels in the film, using SIMS and XPS.

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AF-MoP-16 Expanding the Zinc Precursor Toolbox for Thermal ALD of ZnO, ***Jorit Obenlüneschloß,*** Leibniz Institute, IFW Dresden, Germany*; Jeffrey W. Elam,* Argonne National Laboratory*; Anjana Devi,* Leibniz Institute, IFW Dresden, Germany

Atomic layer deposition (ALD) of ZnO is most commonly based on the diethylzinc (DEZ)/H_2O process, which offers high reactivity and excellent film quality but is associated with significant safety risks due to DEZ's pyrophoric nature. In this work, we systematically evaluate three alternative zinc precursors—bis(3-(N,N-dimethylamino)propyl)zinc(II) ($Zn(DMP)_2$), bis(N-(2-ethoxyethyl)-2-penten-2-on-4-iminate)zinc(II) ($Zn(EEKI)_2$), and ethyl(di(trimethylsilyl)amido)zinc(II) (ZnEt(HMDS))—and benchmark their performance in thermal ALD against DEZ using water as the sole co-reactant.[1]

All four precursors exhibit self-limiting ALD behavior and facilitate the deposition of high-quality ZnO thin films at a common growth temperature of 200 °C. In-situ spectroscopic ellipsometry reveals distinct precursor-specific growth mechanisms, including variations in adsorption behavior, ligand desorption during purge steps, and ligand removal during the water half-cycle. While DEZ shows signatures of partial thermal decomposition, the other precursors retain more intact surface species with steric differences leading to variations in growth per cycle (0.8–2.3 Å) and surface morphology.

Comprehensive ex-situ characterization (XPS, RBS/NRA, AFM, TEM, XRD, and UV/Vis spectroscopy) confirms that all processes yield dense, polycrystalline, near-stoichiometric ZnO films with similar crystallinity and optical band gaps. However, notable differences in surface roughness and nucleation behavior are observed, especially for the bulkier ligand systems $Zn(EEKI)_2$ and ZnEt(HMDS). Importantly, ZnEt(HMDS) enables a previously unreported thermal ALD process with a growth rate comparable to DEZ, while avoiding its extreme pyrophoricity.

These results clearly demonstrate that alternative zinc precursors can deliver ZnO thin films of similar quality to DEZ while providing advantages in safety, growth chemistry, and process flexibility. Expanding the zinc precursor library is therefore an important step toward more robust ALD process design, especially for complex multicomponent oxides and advanced device architectures.

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AF-MoP-17 Comparative Study of Ga Precursors for Low-Temperature PEALD GaN: Trimethylgallium vs. Tris(dimethylamido)gallium, ***Taeyoon Kwon**, Jian Heo, Okhyeon Kim, Hye-Lee Kim, Won-Jun Lee,* Sejong University, Republic of Korea

Gallium nitride (GaN) is essential for next-generation high-power electronics and optoelectronics. However, integrating high-quality GaN films onto temperature-sensitive substrates remains a significant challenge. Although plasma-enhanced atomic layer deposition (PEALD) allows lower processing temperatures than metal-organic chemical vapor deposition (MOCVD) or thermal ALD, selecting the appropriate Ga precursor is essential to optimize growth kinetics and film quality. Previous studies have used trimethylgallium (TMGa) and tris(dimethylamido)gallium (TDMAGa), yet there has been no direct, systematic comparison of their growth behavior and resulting film properties under identical plasma conditions. This study investigates low-temperature PEALD of GaN using alkyl-based TMGa and amido-based TDMAGa in an NH_3 plasma. We analyze the saturation behavior, growth rates, and physical and chemical properties of the deposited films to understand the effect of ligand chemistry. Our results demonstrate that the TDMAGa precursor is significantly more reactive than TMGa, achieving self-limiting growth with shorter exposure times and lower process temperatures. Consequently, films grown with TDMAGa displayed superior material quality, characterized by higher mass density, a higher refractive index, better stoichiometry, fewer carbon and oxygen impurities, and a smoother surface. Cross-sectional analysis of ALD-GaN on n-type GaN substrates revealed a homoepitaxial interface even at 125 °C when using TDMAGa. These results suggest that TDMAGa is the more advantageous precursor for producing high-quality, dense GaN films at low temperatures.Reference[1] S. Banerjee *et al.*, J. Phys. Chem. C 123 (2019) 23214.[2] C. Ozgit *et al.*, J. Vac. Sci. Technol. A 30 (2012) 01A124.

AF-MoP-18 Structural and Electrical Characteristics of Vanadium Oxide Thin Films Grown by ALD Using a Precursor with High Thermal Stability, ***Iksun Kwon**, Seungwoo Lee,* Kyung Hee University, Republic of Korea*; Hyunseok Oh, Donghun Shin, Yongjoo Park,* SK Trichem Co., Republic of Korea*; Woojin Jeon,* Kyung Hee University, Republic of Korea

Vanadium oxide (VO_x) exhibits structure and electrical properties that strongly depend on its oxidation state and crystal structure, making precise control over high-quality thin-film formation critically important. Atomic layer deposition (ALD) enables atomic-scale control of film thickness and composition, offering excellent compositional uniformity and process reproducibility. However, conventional vanadium precursors suffer from limited thermal stability, which restricts the maintenance of self-limiting deposition behavior at temperatures above 200 °C.

In this study, VO_x thin films were deposited by an ALD process using a thermally stable vanadium precursor at deposition temperatures ranging from 150 to 320 °C, and their structural and electrical properties were systematically investigated. At 250 °C, the VO_x films crystallized from an amorphous phase into polycrystalline V_2O_5, with the fraction of the high oxidation state V^{5+} increasing as the deposition temperature increased. In contrast, at 320 °C, partial reduction occurred due to oxygen deficiency induced by the high-temperature process, resulting in an increased contribution of the V^{4+} component. The resistivity of the VO_x films grown on SiO_2 substrates was found to be within the bulk V_2O_5 values reported in the literature. These results demonstrate that a thermally stable precursor–based ALD process enables post-treatment-free control over the crystallinity and electrical conductivity of VO_x thin films.

AF-MoP-19 Engineering Black TiOx: Kinetic Tuning of Ti^{3+} Defects and Polymorph Stability via ALD Pulse Control, ***Jan Leithäuser,*** Heinrich-Buff-Ring 16, Germany*; Jörg Schörmann, Martin Becker, Sangam Chatterjee,* Justus Liebig University Giessen, Germany

"Black" titanium dioxide ($TiO_{x<2}$) has attracted significant attention for photocatalytic and energy storage applications due to its reduced bandgap and high concentration of active Ti^{3+} surface defects. Conventionally, generating these specific defects requires harsh post-treatments like high-pressure hydrogenation. In this work, we improve on a direct, low-temperature Atomic Layer Deposition (ALD) route to synthesize and tune black TiO_x films by exploiting the specific precursor kinetics of the TDMAT/H_2O process [1, 2, 3].

We hypothesize that the concentration of Ti^{3+} defects and consequently the resulting crystal phase can be precisely controlled by manipulating the precursor pulse duration. Using a process temperature of 200 °C, we show that variations in the pulse length allow for the targeted synthesis of specific defect environments.

Preliminary analysis reveals that this defect engineering directly dictates the polymorph stability upon annealing, enabling a tunable shift between anatase- and rutile-dominated modifications. To distinguish between self-limiting ALD growth and parasitic CVD-like decomposition as the origin of these defects, we correlate the structural evolution (GIXRD) with growth rates (GPC) and surface morphology (AFM).

Our results present a novel "kinetic knob" to tailor the stoichiometry and electronic properties of black TiO_x without changing the thermal budget, offering new pathways for defect-enabled functional coatings.

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AF-MoP-20 Studies of Pt ALD Film Conformality and Conductivity with Pillarhall Test Structures, *Jussi Kinnunen,* Chipmetrics Oy, Finland*; Anish Philip, Girish C. Tewari, Mahtab Salari Mehr,* Aalto University, Finland*;* ***Kalle Eskelinen****,* Chipmetrics Oy, Finland*; Thomas Werner,* Chipmetrics GmbH, Germany*; Ramin Ghiyasi,* Aalto University, Finland*; Stefan Polzin,* Chipmetrics GmbH, Germany*; Maarit Karppinen,* Aalto University, Finland

Atomic layer deposition (ALD) of noble metals such as platinum (Pt) is increasingly relevant for advanced device applications, yet remains challenging due to high precursor cost, narrow process windows, and limitations of conventional metrology for assessing conformality in high aspect ratio (HAR) features. In this work, we present the first demonstration of combined conformality and electrical characterization of Pt ALD films using the electrical test structure patterning enabled by PillarHall technology. The structure is based on pillar-stabilized large-area membrane that can be selectively removed by tape lift-off after the deposition. This membrane removal leaves controlled narrow line of thin film with probe/solder pads at each end, enabling direct electrical contacting without additional processing.

Pt thin films were deposited in a thermal ALD reactor (Picosun R100) using $MeCpPtMe_3$ and O_2 at 300 °C, based on a process previously optimized for planar substrates [1]. To enable reliable electrical probing while minimizing disturbance to the ALD process a thin dielectric precoating of 5 nm Al_2O_3 was introduced on top of the native oxide. Film thickness and conformality were evaluated optically using ellipsometry. For Pt thicknesses up to 25 nm, changes in optical parameters are sensitive to film growth, enabling thickness measurement along the lateral high aspect ratio (LHAR) channel. Beyond this range, ellipsometric response saturated, highlighting a fundamental limitation of optical metrology for thicker metallic films. In parallel, four-probe resistance measurements were performed on the same LHAR5 chips, enabling direct correlation between electrical properties and film thickness. The measured resistance followed the expected thickness dependence, increasing with decreasing Pt thickness, while temperature-dependent measurements showed metallic behavior, with resistance increasing with temperature in the range 100-400 K.

The current research demonstrates that the LHAR5 electrical test structure provides a controlled and robust platform for studying highly conductive films, enabling reliable measurements over wide temperature ranges and penetration depths. The methodology provides a practical route to study noble metal ALD processes in HAR structures and opens pathways for future work combining electrical, optical, and nanoscale characterization, including AFM-based conductivity mapping and SEM/EDS analysis.

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AF-MoP-21 Growth Rate of ALD Al_2O_3 on Nanocellulose – Quantification Technique and Analysis, ***Hugo Patureau,*** SIMAP, Grenoble-INP, CNRS, France*; Erwan Gicquel,* Cilkoa, France*; Frédéric Mercier, Elisabeth Blanquet, Arnaud Mantoux,* SIMAP, Grenoble-INP, CNRS, France

Cellulosic products have emerged as a solution to plastics in the packaging industry due to being recyclable and bio-degradable. Recent research has shown that functionalising cellulose substrates with Al_2O_3 deposited by atomic layer deposition (ALD) improves their barrier properties and grants hydrophobicity. While research on the topic is mainly focused on functional properties, relating these properties to film thickness is challenging, due to the fibrous nature of the substrate. Consequently, thickness on cellulosic substrates is often estimated from silicon wafers processed under identical conditions. ALD is known to be substrate dependent, making this approach unsatisfactory. This work demonstrates a strategy to quantify ALD Al_2O_3 on nanocellulose substrates. Quantification is achieved through acid digestion and inductively coupled plasma mass spectrometry (ICP-MS), and a calibration curve X-Ray fluorescence (XRF) is established (Figure 1). This allowed rapid, fully quantitative, and non-destructive measurements. This method was then used to investigate the Al_2O_3 ALD window on nanocellulose, saturation curves and insights on early stage ALD growth on the substrates. Findings indicate a substrate-enhanced growth rate on nanocellulose, with the steady state growth per cycle (GPC) significantly greater on nanocellulose, than on silicon wafers processed under identical conditions (Figure 2). These results highlight the importance of quantifying growth directly on the cellulosic substrates.

AF-MoP-22 Self-Assembled Monolayers of Phosphorus–Nitrogen Cages, *Justin Lomax,* Western University, Canada*; Michael-John Treanor,* St. Andrews, UK*; Michael Land,* Dalhousie University, Canada*; Wai-Tung Shiu, Bentley Jordan,* Western University, Canada*; Saurabh Chitnis,* University of Victoria, Canada*; Christopher Baddeley,* University of St. Andrews, UK*;* ***Paul Ragogna****,* Western University, Canada

Self-assembled monolayers (SAMs) are organized films that spontaneously form when molecules attach to a surface and arrange into ordered structures. SAM assembles and the modification of the surface are determined by the nature of the surface-binding group, the architecture of the backbone, and the terminal functionality. The molecule-surface interaction has a profound impact in areas such as molecular electronics and protective coatings. Carboxylic acids, thiols, silanes, phosphonic acids, and carbenes have been widely used for SAM coatings, while limited effort has been directed toward exploring alternative surface ligands, especially those based on inorganic scaffolds. The phosphaza-bicyclo[2.2.2]octane core is symmetrical and contains P(III) centers at axial positions within a rigid three-dimensional architecture. Its modular synthesis enables control over volatility and reactivity while preserving a chemically robust framework. We have establishedP_2N_6 as a new molecular platform for SAMs. By demonstrating deposition and selective adsorption on metals, we reveal the ability for monolayer formation that expands the precursor design space for deposition processes. This represents the first time that resilient, P-based SAM has been identified. Details of careful quartz crystal microbalance (QCM) experiments, molecular layer deposition (MLD) processes and scanning tunneling microscopy results will be presented.

AF-MoP-23 Mophological Analysis of ALD HZO Thin Films Using Cp-Based Hf/Zr Precursors, ***Chang Ho Lee,*** CN1 Co., Ltd, Republic of Korea

In recent years, extensive research has been conducted on application of doped-HfO_2 as high-k dielectric materials in advanced electronic devices such as dynamic random-access memory (DRAM), ferroelectric field-effect transistors (Fe-FETs), and ferroelectric junction transistors (FJTs). Among these materials, ZrO_2-doped HfO_2, specifically $Hf_{0.5}Zr_{0.5}O_2$ (HZO), has attracted significant attention as a promising alternative dielectric for DRAM capacitor applications. HZO exhibits various crystalline phases depending on dopant concentration and thermal conditions, including the tetragonal phase with a high dielectric constant and the non-centrosymmetric orthorhombic phase, which is associated with ferroelectric behavior. In this study, HZO thin films were deposited using an atomic layer deposition (ALD) process with Cp-based Hf and Zr precursors at low temperatures ranging from 250 to 350 °C. The morphological characteristics and thickness uniformity of the deposited HZO films were evaluated using atomic force microscopy (AFM) and X-ray reflectivity (XRR). The crystalline structure and phase distribution were analyzed by X-ray diffraction (XRD), while the microstructural features and interfacial properties were further investigated using transmission electron microscopy (TEM). This systematic analysis provides insight into the effects of deposition temperature on the morphological and structural properties of low-temperature ALD-grown HZO thin films, offering a fundamental understanding for process optimization in high-k dielectric applications.

AF-MoP-24 Indium Precursor Development for High Quality InOx-based Film for Future Oxide Semiconductor Applications, ***Nana Okada****, Atsushi Sakurai, Ryota Fukushima, Keisuke Takeda, Masaki Enzu,* ADEKA CORPORATION, Japan*; Tomoharu Yoshino,* ADEKA KOREA CORPORATION, Korea (Democratic People's Republic of)*; Atsushi Yamashita, Yoshiki Oe, Yutaro Aoki,* ADEKA CORPORATION, Japan*; Akihiro Nishida,* a.nishida@adeka.co.jp

Indium-based oxide semiconductors (OS) such as In_2O_3[1)], IGZO[2)], IGO[3)], IWO[4)], and ITO[5)] have garnered significant attention for future logic and memory applications due to low leakage, high mobility, and BEOL compatibility as channel materials. As the OS film is expected to be grown on a 3D architecture different from a Si crystal, there is a strong demand for ALD indium precursors which enable conformal deposition, precise thickness and compositional control. As a result, we have focused on indium precursor development for high temperature ALD processing to produce high quality InOx-based thin films with a very small amount of organic impurities.

Here we present DKI-6 which is a heteroleptic indium precursor with bulky *β*-diketimine and methyl ligands (Fig.1). It is a liquid at room temperature, has a 1 torr vapor pressure at 105°C, and decomposed at 328°C (onset, DSC). DKI-6 successfully produced smooth and high quality In_2O_3 films with a GPC of 0.54 Å/cycle on an SiO_2 substrate using O_3 ALD processing at 300°C (Fig.2 and Fig.3). Interestingly, we found Si diffusion into the In_2O_3 film from

the SiO_2 underlayer using H_2O ALD at 300°C, which could imply lower density In_2O_3 film growth with lower GPC of 0.40Å/cycle (Fig.4).

In conclusion, we successfully obtained ALD In_2O_3 films using DKI-6 and O_3 or H_2O coreactants at 300°C with the reasonable GPC. This result will extend into further development of various kinds of InOx-based OS thin films.

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AF-MoP-25 Novel Tantalum Precursor for High-Quality Ta_2O_5 Thin Films by Atomic Layer Deposition, ***Luis Misal***, *Sunao Kamimura,* Air Liquide Laboratories, Japan*; Nicolas Blasco,* Air Liquide, France

1. INTRODUCTION

Tantalum(V) oxide (Ta_2O_5) is a critical material for advanced optical coatings and next-generation DRAM capacitors due to its high refractive index, low optical absorption, and high dielectric constant [1]. Atomic Layer Deposition (ALD) is the preferred method for depositing highly uniform and conformal films required for these applications, especially on curved substrates. However, common tantalum precursors (e.g. TBTDET, TBTEMT) often lead to films with high carbon and nitrogen contamination [2,3], which is detrimental to thin film performance. This work introduces a novel tantalum precursor, RosiTa™, for the ALD of high-quality Ta_2O_5 thin films.

2. EXPERIMENTAL

A novel liquid Ta precursor, RosiTa™ was synthesized and characterized. Its thermal properties and volatility were evaluated by thermogravimetric analysis (TGA). RosiTa™ has good volatility (1 Torr at 106 °C, Fig. 1), and presents long-term thermal stability with no decomposition detected after 12 weeks at 110°C, making it suitable for ALD applications. Ta_2O_5 thin films were deposited by thermal ALD on silicon substrates using RosiTaTM as tantalum source and ozone (O_3) as the oxygen source. The deposition was carried out in a temperature range of 200-350 °C, with a GPC ~0.48 Å/cycle (ALD window 275-300 oC). The resulting films were analyzed by X-ray photoelectron spectroscopy (XPS) (Fig. 2) to determine their composition and purity. The ALD process using RosiTa™ and O_3 yielded highly conformal Ta_2O_5 thin films with excellent step coverage on high-aspect-ratio structures (Fig. 3).

A key finding of this work is the exceptionally low nitrogen and carbon contamination in the Ta_2O_5 films grown with RosiTa™. This is a significant improvement over other precursors (e.g. TBTDET, TBTEMT) and is a critical advantage for different applications.

3. SUMMARY

The novel volatile tantalum precursor, RosiTa™ has been successfully used for the ALD of high-quality Ta_2O_5 thin films. RosiTa™ stands out due to its excellent thermal stability and the ability to produce highly conformal Ta_2O_5 films with nitrogen and carbon contamination below the detection limit for XPS. These features make RosiTa™ a very promising precursor for demanding ALD thin film applications.

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AF-MoP-26 Growth and Characterization of Bi_2O_3 Thin Films Prepared by Atomic Layer Deposition from $Bi(O^tBu)_3$, ***Hyo Jin Park,*** Sookmyung Women's University, Republic of Korea*; Injeong Ryu, Gwon Deok Han,* Sookmyung Women's University, Republic of Korea

High-bandwidth memory (HBM) is essential for AI-based computing, necessitating the development of high-performance dynamic random access memory (DRAM). DRAM devices are evolving toward higher efficiency through higher integration, which inevitably requires reducing the physical size of DRAM capacitors. Therefore, the development of next-generation high-k dielectric materials that maintain sufficient capacitance without compromising leakage current levels is crucial. In this study, we investigated bismuth oxide (Bi_2O_3) films deposited by atomic layer deposition (ALD) as a promising high-k candidate material for future DRAM capacitors. We explored the applicability of bismuth tertiary-butoxide ($Bi(O^tBu)_3$), a precursor with limited research experience in ALD processes. Furthermore, we compared the structural and electrical properties of films deposited using different reactants (O_2 and O_3). The comparative analysis revealed significant differences in growth behavior, crystallinity, and interface quality depending on the choice of reactants. Additionally, the energy bandgap and dielectric constant were evaluated to determine the material's suitability for scaled capacitor nodes. This presentation explores the potential of ALD-grown Bi_2O_3 as a viable dielectric solution for next-generation DRAM technology.

AF-MoP-27 Effect of Temperature and Oxidant on Structural, Chemical, Optical and Morphological Properties of ALD Grown Cobalt Oxide, *Swapnil Nalawade, Ahmed Wasif Mustakim,* ***Shyam Aravamudhan,*** North Carolina A&T State University

Cobalt oxide thin films are of significant interest for applications in electrochemical energy storage, catalysis, gas sensing, and emerging electronic and neuromorphic devices, where precise control over phase, stoichiometry, and surface morphology is critical. In this work, we report a comprehensive study of the growth behavior and property evolution of cobalt oxide thin films deposited by atomic layer deposition (ALD) using cobalt(II) ethylpropanimidamidato as the metal precursor and ozone or water vapor as the oxidant, with particular emphasis on the role of deposition temperature. Saturated ALD growth was achieved within a temperature window of 180–260 °C. Film composition and oxidation states were analyzed using X-ray photoelectron spectroscopy (XPS), while crystallographic structure was examined by X-ray diffraction (XRD). Atomic force microscopy (AFM) revealed a strong dependence of surface morphology on deposition temperature. Raman spectroscopy confirmed that films deposited at lower temperatures exhibit a mixed-phase composition consisting of Co_3O_4 and CoO, whereas higher temperatures promote phase purity. Spectroscopic ellipsometry was employed to determine film thickness and extract temperature-dependent optical constants. This work demonstrates ALD as a highly repeatable and scalable pathway for depositing uniform cobalt oxide thin films with tunable phase composition and optical properties, enabling materials optimization for application-specific integration.

AF-MoP-28 Hybrid 1D/3D Analytical Step–Coverage Modeling for Inhibitor-Free Superconformal Molybdenum Gap-Fill, ***David Mandia***, *Lee Brogan, Matthew Griffiths, Jennifer O'Loughlin Petraglia,* Lam Research Corporation

Void–free metallization in sub–20 nm features requires predictive control of conformality while avoiding etch–dominated failure. Depending on the application, a conformal, bottom-up (selective), or superconformal step coverage is required.[1] Herein, an analytical step coverage (SC) function is derived using 1D trench-filling kinetics and employed in conjunction with Lam's SEMulator3D® to understand and predict the regimes of subconformality, conformality, and superconformality for Mo gap-fill. Our model system is the $MoCl_5/H_2$ ALD process, which also contains self-etching pathways that need to be considered. The $MoCl_5/H_2$ chemistry is described using two competing surface pathways: (1) deposition, $MoCl_5 + 5/2\ H_2 \rightarrow Mo + 5HCl$, with rate with rate $R\text{depα}PAPB5/2$, and (2) self–etch, $2MoCl_5 + Mo \rightarrow MoCl_4 + Mo_2Cl_6$, with rate with rate $R\text{depα}PAPB5/2$. The stoichiometric flux terms for 1D Knudsen trench filling are mapped onto the 2D/3D SEMulator3D model to understand $MoCl_5/H_2$ flux regimes that lead to a SC function which is <1 (subconformal), ≈1 (conformal), ≤0 (stalled/over-etch), or >1 (superconformal). In this feature-scale growth physics modeling approach, we present the transition between these regimes using experimental results obtained from internal high-aspect-ratio structure data. The 1D model provides fast, physics–transparent process boundaries, while SEMulator3D® modeling propagates these conditions into realistic 2D/3D profiles, enabling accelerated and robust process development for Mo interconnects.

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AF-MoP-29 Low Temperature ALD Vanadium Nitride Using Anhydrous Hydrazine, *Dan Le, Austen Adams,* ***Lorenzo Diaz,*** RASIRC*; Dushyant Narayan, Minjong Lee, Thi Thu Huong Chu,* University of Texas at Dallas*; Adrian Alvarez,* RASIRC*; Jiyoung Kim,* University of Texas at Dallas

As device dimensions continue to shrink, TiN as the electrode material for advanced devices faces critical limitations, including high resistivity and increased leakage current density arising from its relatively low work function (~4.2 eV) [1,2]. These constraints drive the need for improved electrode materials for the next scaled technological node. Vanadium nitride (VN) is a promising candidate owing to its favorable characteristics,

including a high work function (up to ~5.5 eV), low resistivity, and notable mechanical properties [3].

In this work, we focus on the development of a BEOL-compatible, low-temperature thermal ALD process for vanadium nitride (VN) thin films, employing BRUTE® anhydrous hydrazine (N_2H_4) as the nitrogen source to enable integration as a potential electrode material for next-generation devices. Using the anhydrous N_2H_4 source, uniform VN thin films were successfully deposited at temperatures as low as 250 °C, achieving a growth rate of ~0.05 nm per cycle and a film density of ~5.40 g/cm^3. XPS analysis of a 10 nm VN film deposited at 250 °C confirmed successful nitride formation at this reduced temperature, although ~15 at. % oxygen contamination was detected within the film. The as-deposited VN films exhibited a resistivity as low as ~600 μΩ·cm, with less than 5% variation across the test wafer, indicating good film uniformity and electrical consistency. MOS capacitors will be fabricated to further evaluate the electrical properties of the deposited films. Detailed experimental procedures and comprehensive characterization results will be discussed.

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AF-MoP-30 Non-Destructive Characterization of Alumina Film Thickness and Fractional Coverage Utilizing XPS and StrataPHI for Metrological Analysis*, **Amy Ferryman**, Norb Biderman, Kateryna Artyushkova,* Physical Electronics

Atomic layer deposition (ALD) is widely used due to its precise deposition capabilities, allowing for the creation of very thin, conformal, and high-quality films on the nanometer scale. These films are ideal for applications requiring precise barrier layers, passivation layers, or protective coatings in complex geometries, particularly in microelectronics, sensors, and medical devices. ALD deposition of alumina offers several advantages, including uniform coating on complex 3D structures, precise thickness control, high purity, and suitability for sensitive substrates due to its low deposition temperature. The self-limiting behavior of ALD cycles allows for controllable film growth in which a homogenous film can be achieved at the lowest film thickness. To control the thickness in a range of few nanometers, it is important to understand the interaction between the reactants and substrate during the nucleation period, or the first few cycles. X-ray photoelectron spectroscopy (XPS) is a well-established technique for non-destructive analysis of the chemical composition of thin layers and interfaces. By analyzing a material at varying takeoff angles between the sample and analyzer, angle dependent XPS (ADXPS) can be utilized to probe the thickness and chemical composition of thin films without creating ion beam-induced damage associated with destructive sputter profiling. The spectral results obtained by ADXPS can be furthered evaluated by *Strata*PHI, a software product designed by Physical Electronics, to calculate not only the thickness of thin films but also provide an estimate of fractional coverage, which is of great importance for high-throughput metrology of thin-film structures. This presentation will highlight the benefits of utilizing angle dependent XPS in combination with StrataPHI modeling software to non-destructively characterize and simultaneously calculate the layer thickness and fractional coverage of a series of aluminum oxide films deposited on glass substrates throughout the nucleation period by the ALD process.

AF-MoP-31 Effect of Pnictogen Hydrides XH_3 (X=P, As, Sb) Doping on Silicon Deposition: A First-Principles Study*, **Rabi Khanal**, Raymond Joe, Anthony Dip,* Tokyo Electron America, Inc.

Pnictogen hydrides, such as PH3, have been used to dope silicon (Si) surfaces during the fabrication of quantum electronic devices with atomic-scale precision. Additionally, dissociative adsorption of XH3 is believed to effectively alter surface energetics and morphology during film growth, enabling control over dopant concentration and spatial distribution within the film. Once the dopant is incorporated into the surface, the growth of silicon can be affected by the dopant's concentration as well as its chemical and physical properties. Developing a fundamental understanding of dopant characteristics and growth processes is essential to ensure and improve a priori prediction of suppressed or enhanced growth rates and uniformity in critical Si film deposition for many applications, including logic, NAND, and DRAM devices.

In this study, we first performed ab initio molecular dynamics (AIMD) simulations of SiH4 (a Si precursor) deposition on the Si(001) surface at various dopant concentrations. Our simulations show that dilute dopant concentrations at the surface, in the absence of hydrogen, do not significantly affect SiH4 deposition. To have a meaningful impact on Si film growth, an adequate amount of dopants must be present on the surface. We also analyzed the detailed reaction mechanism of SiH4 deposition on a surface using a dimer model at the density functional theory level with dissociatively adsorbed XH3. For the XH3-incorporated Si(001) surface, we considered the most widely used dissociative adsorption states: XH2+H, XH+2H, and X+3H. Our results indicate that the energy barrier for silane (SiH4) deposition increases in the presence of XH3 compared to a surface without dopants, implying slower film growth. The magnitude of the energy barrier—and its effectiveness in limiting film growth—strongly depends on the state of adsorbed XH3 (XH+2SiH versus X+3SiH) on the Si surface. Furthermore, we will discuss how surface-site dependence influences Si adsorption relative to dopant location and chemistry (e.g., As, Sb, P), aiming to link these effects to intrinsic dopant properties, such as electronegativity and atomic radius.

AF-MoP-32 Rutile TiO_2 Thin Films Grown by Remote Plasma ALD on RuO_2 Seed Layers for Advanced Capacitor Structures*, **Yongwoon Jang**, Jiwon Kim, Byungwook Kim, Minkyun Kang, Hyeonwu Nam, Changbun Yoon,* Tech University of Korea

As DRAM capacitor structures continue to scale down, achieving ultrathin dielectric films with high capacitance density and low leakage current has become increasingly important. Rutile-phase TiO_2 is a promising high-k dielectric material due to its intrinsically high dielectric constant; however, stabilizing the rutile phase in ultrathin films remains challenging because of phase instability and interfacial degradation.

In this study, RuO_2 bottom electrodes were fabricated by reactive RF sputtering using a metallic Ru target, with oxygen flow ratios of 20%, 30%, and 40% and substrate temperatures ranging from 300 to 500 °C. These parameters significantly influenced the oxidation state and crystallinity of the RuO_2 films, which in turn affected the subsequent growth behavior of TiO_2. TiO_2 thin films were deposited on the RuO_2 electrodes using remote plasma plasma-enhanced atomic layer deposition (PEALD), and the impact of RuO_2 seed layer crystallinity on TiO_2 phase evolution was systematically investigated. Post-deposition oxygen annealing was additionally employed to enhance rutile phase stability.

As a result, highly crystalline rutile-phase TiO_2 thin films were successfully obtained, exhibiting an equivalent oxide thickness below 1 nm and leakage current densities lower than 10^{-5} A cm^{-2}.

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AF-MoP-33 2.5 Å/cycle PEALD of SiO_2 Using a Tri-Silyl Precursor for Advanced Gap-Fill Applications*, **Wonyong Koh**, Byung-Kwan Kim, Won-Jeong Hwang, Su-Yeon Lee, Seung-Gyun Hong, Jin-Sik Kim, Hyun-Kyu Ryu,* UP Chemical Co., Ltd., Republic of Korea

High-quality SiO_2 films were deposited by plasma-enhanced atomic layer deposition (PEALD) using hexamethyldisilylaminodimethylaminosilane (HMDMS, $(Me_3Si)_2N$-SiH_2-NMe_2) and O_2 plasma at 550°C, achieving growth per cycle (GPC) of 2.5 Å/cycle. For comparison, thermal ALD process using the same precursor with O_3 at 700°C reported GPC of 3.0 Å/cycle, excellent electrical properties and good conformity [1]. Secondary ion mass spectrometry (SIMS) analysis revealed that PEALD SiO_2 films exhibit comparable C and N impurity levels to a thermally grown oxide film, with only 30% higher H content. The wet etch rate in 100:1 diluted HF was 1.5 Å/s, approximately twice that of thermal oxide (0.8 Å/s), indicating excellent film density. Transmission electron microscopy demonstrated outstanding conformality, with 98.6% step coverage for 10-nm-thick films on 20:1 aspect ratio hole patterns. Electrical characterization of 20-nm-thick PEALD SiO_2 films showed low leakage current density (0.7 nA/cm^2 at -2 MV/cm) and Fowler-Nordheim tunneling behavior at high electric fields, confirming high-purity, defect-free dielectric properties comparable to thermal SiO_2 ALD at 600-700°C [1]. The combination of high GPC, excellent conformality, and superior electrical properties makes this PEALD process promising for dielectric gap-fill applications in advanced semiconductor devices, particularly 3D NAND memory.

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AF-MoP-34 Non-Pyrophoric Zinc Precursor AP–MDS™131: Extended ALD Window and Benchmarking Against Diethylzinc, ***Lukas Mai,*** *Jan-Lucas Wree,* EMD Electronics, Germany*; Bhushan Zope, Randall Higuchi, Khang Ngo,* EMD Electronics*; Holger Heil,* EMD Electronics, Germany*; Sergei Ivanov,* EMD Electronics

Atomic layer deposition (ALD) of ZnO is a key enabling technology in advanced electronic and optoelectronic devices, but the benchmark precursor diethylzinc (DEZ) shows limited thermal stability in the higher temperature regimes required for next–generation processes. In this work, we evaluate a new zinc precursor, AP–MDS™ 131, with the dual objectives of improving high–temperature process robustness relative to DEZ (>150 °C for H_2O and >250 °C for O_3) and achieving lower, more controllable growth rates within well–defined ALD windows. Thermogravimetric and calorimetric data indicate that AP–MDS™ 131 combines usable volatility with enhanced thermal stability, supporting operation at elevated temperatures without precursor decomposition under ALD conditions; moreover, AP–MDS™ 131 is non–pyrophoric, in contrast to pyrophoric DEZ, which has clear handling and safety advantages.

Process studies show that both DEZ and AP–MDS™ 131 exhibit no detectable decomposition on SiO_2 under the tested high–temperature conditions, but they differ in desorption behavior and process windows. For O_3–based ZnO ALD, literature and internal data indicate that DEZ lacks a clear high–temperature ALD window due to strong desorption, whereas AP–MDS™ 131 provides a distinct high–temperature ALD window with only limited desorption at even higher temperatures. At representative conditions, both precursors display saturation behavior consistent with self–limiting ALD growth.

With H_2O as co–reactant, AP–MDS™ 131 enables an additional ALD window at intermediate temperatures, with well–defined saturation of both precursor and reactant and no evidence of decomposition on SiO_2. In comparison, DEZ/H_2O operates at lower temperatures and yields higher growth per cycle, whereas AP–MDS™ 131/H_2O provides substantially reduced growth rates within its window—a central development target to enable highly controlled, thickness–tunable processes. Across all investigated conditions, ZnO films from both precursors exhibit carbon below detection, near–stoichiometric O/Zn ratios, and high densities, demonstrating that the improved high–temperature capability and reduced growth rate of AP–MDS™ 131 are achieved without compromising film quality.

Overall, AP–MDS™ 131 expands the usable ALD window for ZnO toward higher temperatures for both O_3 and H_2O processes compared to DEZ, while offering lower, more manageable growth rates, non–pyrophoric handling, and maintaining high film purity and near–ideal stoichiometry—making it a strong candidate for tightly controlled ZnO ALD in microelectronics and display technologies.

AF-MoP-35 Indium Precursors Targeting ALD of Indium Films, ***David Ermert,*** Entegris, Inc.

Multicomponent metal-oxide thin-film transistors (TFTs) are promising candidates for next-generation memory components owing to their high electron mobility and low-leakage properties. For example, Indium-Gallium-Zinc-Oxide (IGZO) films are candidates for channel materials in 3D DRAM. Given the aggressive features of proposed device architectures, ALD of IGZO type films will be required for vertical scaling. The incumbent precursor for many indium-containing films is $InMe_3$, a pyrophoric solid which presents physical challenges and limitations to widespread adoption and underscores the need for novel, safe, and suitable precursor chemistry to accommodate ALD growth.

We report, herein, on physical properties and thermal analysis of a structurally diverse collection of indium compounds, including known and novel compositions. We also present varied synthetic approaches to organometallic indium compounds with an emphasis on non-pyrophoric routes and reagents. In addition, we discuss In_2O_3 film growth from a newly developed non-pyrophoric organometallic indium precursor.

AF-MoP-36 Imaging Spectroscopic Ellipsometry as a Wafer-Scale Metrology Tool 2D TMDs, ***Mangesh Diware,*** Park Systems Inc*; Michael Curtis,* Micron School of Materials Science and Engineering, Boise State University*; Ashton Enrriques,* Park Systems Inc*; David Estrada,* Micron School of Materials Science and Engineering, Boise State University

Imaging spectroscopic ellipsometry (ISE) combines spectroscopic sensitivity with spatially resolved measurements, providing a powerful, non-destructive approach for characterization of ultra-thin materials. In this work, ISE is applied to wafer-scale MoS_2 and WS_2 films deposited by atomic layer deposition, enabling simultaneous mapping of thickness and optical properties with micrometer-scale spatial resolution. This capability is well suited for deposition process development and uniformity assessment.

ISE measurements were performed over a broad energy range to capture excitonic and interband transition features characteristic of monolayer and few-layer transition metal dichalcogenides. The extracted dielectric functions exhibit well-defined excitonic resonances consistent with reported literature values, while wafer-scale thickness maps reveal both uniform regions and localized deviations. These results demonstrate the capability of ISE as a quantitative, high-throughput optical metrology technique for ultrathin films. The demonstrated approach is applicable to both research and manufacturing environments, providing scalable characterization of ultra-thin semiconductors.

AF-MoP-37 Developments in low growth rate aluminum oxide ALD with AP-MDS™ 026 and AP-MDS™ 027, ***Jan-Lucas Wree,*** *Lukas Mai,* EMD Electronics, Germany*; Bhushan Zope,* EMD Electronics, USA*; Randall Higuchi,* EMD Electronics*; Khang Ngo,* EMD Electronics, USA*; Holger Heil,* EMD Electronics, Germany*; Sergei Ivanov,* EMD Electronics, USA

Precise thickness control in multilayer stacks motivates the development of aluminum oxide (Al_2O_3) atomic layer deposition (ALD) processes with intrinsically low growth-per-cycle (GPC). We evaluated new organoaluminum precursors—AP-MDS™ 026 and AP-MDS™ 027—against conventional chemistries (e.g., TMA, TDMAA, aluminum sec-butoxide, $Al(mmp)_3$) to identify process windows that reliably deliver low GPC while maintaining surface saturation, film uniformity and high conformality.

Across co-reactants, both H_2O- and O_3-based processes exhibited clear precursor saturation behavior, with O_3 generally yielding lower deposition rates than H_2O under otherwise comparable process conditions.

Benchmark GPCs spanned approximately 1.0–1.2 Å/cycle for TMA/O_3 and 0.8–1.0 Å/cycle for TDMAA/H_2O or O_3, decreasing to 0.4–0.5 Å/cycle for aluminum sec-butoxide/O_3 (<250 °C) while water processes always yield growth rates above 0.6 Å/cycle. Notably, AP-MDS™ 027 paired with O_3 enabled the lowest GPC regime observed, ~0.19–0.26 Å/cycle at 250–300 °C, while AP-MDS™ 026/H_2O and AP-MDS™ 027/H_2O both yielded ~0.6 Å/cycle under the measured conditions rendering them as suitable candidates for lowering the growth rate of aluminum oxide ALD with both ozone and water as co-reactants.

Early-cycle behavior (i.e. growth delay) was strongly precursor- and co-reactant-dependent and substrate effects on growth were more pronounced for AP-MDS™ 026 and AP-MDS™ 027 compared to conventional precursors. Moreover, process optimization emphasized the benefits of a less reactive, sterically bulkier yet volatile and thermally stable precursor for controllable Al_2O_3 ALD.

Collectively, these results establish O_3-driven and H_2O-driven AP-MDS™ 026 and AP-MDS™ 027 as a robust route to sub-0.3 Å/cycle and ~0.6 Å/cycle Al_2O_3 ALD, respectively. Our processes demonstrate that precursor selection, co-reactant and substrate choice provide orthogonal controls to tune nucleation and growth for angstrom-level thickness control in complex multilayer architectures.

AF-MoP-38 Inline XPS and Raman Metrology for Evaluating Integrity of Selectively Deposited Graphene During Thin Film Deposition, *Dominic Esan, Kitty Kumar, Ahmad Al-Kukhun, Wing-Shun Lam, Sisi Cao,* Intel Corp.*; **Ganesh Vanamu,*** Nova Ltd.*; Yinon Katz, Haim Prigozin, Lior Neeman, Tamar Hess,* Nova Ltd., Israel*; Sumegha Godara, Roland Barbosa,* Nova Ltd.

As semiconductor devices shrink below 2-nm, copper (Cu) interconnect reliability is increasingly constrained by electromigration and diffusion into surrounding dielectrics. Traditional capping layers such as Cobalt provide protection but add unwanted parasitic resistance and limit further scaling. Graphene offers a promising alternative due to its atomic thickness and high electrical conductivity [1-2]. However, integration of graphene in the back-end-of-line stack requires protection of graphene structure and properties from the downstream processing steps such as thin film deposition, etching, etc. This work investigates the impact of plasma

assisted (DL1) and thermally grown (DL2) dielectric thin films on the graphene composition, thickness, and hybridization states using VeraFlex (XPS) and Elipson (Raman) metrology tools, developed by Nova Ltd. The study identifies key process–structure correlations and strategies to enable reliable graphene–dielectric integration in advanced interconnects.

Sensitivity of many graphene attributes, like layer-number identification, structural quality and defects, makes Raman spectroscopy a promising tool for process development [3-4]. Plasma deposition, which uses ions bombardment of the surface, can lead to significant damage to the substrate layers [5]. Here, we examine the extent of this effect in multiple scenarios. The Raman spectra reveals that the thermal DL2 layer deposited directly over Graphene had minimal impact on the Graphene's spectrum, while a plasma DL1 layer changed significantly. The significant change in graphene quality by DL1 is evident from the drop of the 2D peak intensity, indicating reduction in the quality of the graphene film as compared to pristine graphene and graphene_DL2 sample (Fig.1). On patterned wafers, the graphene quality deteriorates when exposed to the plasma deposition even when protected by one or few thermal layers. This damage is reflected in the reduction of the 2D peak amplitude and peak broadening. However, as the number of thermal layers increases, the extent of this damage diminishes (Fig.2), indicating DL2 can offer partial protection against plasma-induced damage. Complementary XPS analysis confirmed uniform deposition of both DL1 and DL2. Compared to the sp^2/sp^3 ratio derived from the C1s spectra of pristine graphene (Fig.3a), DL1 processing leads to a reduction in the sp^2/sp^3 ratio, indicating increased disorder, whereas optimized DL2 layers restore a higher sp^2 fraction, consistent with reduced damage (Fig.3b). Further, the results demonstrate uniform thermal DL2 growth and a clear correlation between DL2 thickness and graphene protection (Fig.4). These findings provide process-level insight into dielectric–graphene interactions and establish guidelines for integrating graphene with dielectric thin films in advanced interconnects.

AF-MoP-39 Design of Experiments Approach to Controlling ALD-Grown Hafnium Oxide Film Properties, *Emily Wang, Tarun Maredla, Iryna Golovina, David Barth,* ***Lucas Barreto,*** University of Pennsylvania

Hafnium oxide (HfO_x) is a versatile material with applications across multiple technological fields. Its compatibility with CMOS processes enables integration into microelectronic devices, where its high dielectric constant makes it an attractive alternative to silicon dioxide. In addition, hafnia exhibits a high refractive index, which is advantageous for optical and protective coating applications, while its excellent thermal stability supports use in high-temperature environments.

Atomic layer deposition (ALD) provides precise control over the growth of HfO_x thin films, with process parameters strongly influencing the deposition rate and resulting film properties. In this work, we investigate the effects of deposition temperature, precursor pulse time, and purge time on the properties of thermal ALD-grown HfO_x films. A full-factorial design of experiments is employed to systematically evaluate how these parameters affect growth per cycle, refractive index, and film density.

We use tetrakis(dimethylamido)hafnium (TDMAH) as the metal precursor, and H_2O as the oxygen source. We measure the film refractive index using spectroscopic ellipsometry and the film density using X-ray reflectivity. The analysis enables identification of the statistically relevant factors and how factor interactions influence each response, providing optimal ALD process conditions to tune HfOx deposition.

Atomic Layer Etching
Room Tampa Bay Salons 5-9 - Session ALE-MoP
Atomic Layer Etching Poster Session

ALE-MoP-1 Low-Temperature Isotropic ALE of Oxides for 3D Nanostructures and Quantum Device Fabrication, ***Maria Efthymiou Tsironi,*** LBNL

Atomic layer etching (ALE) with high selectivity, low damage, and minimal thermal budget is increasingly important for advanced microelectronics and quantum devices. In this work, we present a plasma-based ALE approach for SiO_2 and Al_2O_3 that enables controlled, isotropic material removal using sequential SF_6, trimethylaluminum (TMA), and low-power Ar plasma exposures. The processes are designed to operate at room temperature or modest heating, expanding the accessible parameter space for temperature-sensitive substrates.

For SiO_2, we implement a near-room-temperature ALE sequence using alternating SF_6 and Ar plasma steps. Ellipsometry measurements indicate self-limiting behavior in both half-reactions, with no measurable etching during isolated SF_6 or plasma exposures and an expected etch-per-cycle (EPC) of ~1 Å. A defined temperature and plasma-power window supports stable etching and strong selectivity to underlying Si, making the process suitable for applications where substrate preservation is critical.

We further extend this strategy to Al_2O_3 by introducing a TMA pulse following SF_6 surface fluorination. This fluorination–ligand-exchange mechanism enables isotropic removal of the modified layer, yielding an EPC of ~0.9 Å/cycle at 150 °C. The process provides reliable etching on both horizontal and vertical surfaces, demonstrating applicability to 3D structures. XPS, AFM, and SEM confirm reduced surface roughness and uniform material removal, consistent with self-limited etching.

Together, these results establish a versatile ALE platform capable of high-precision, low-temperature oxide etching. The approach offers a safer and more controllable alternative to HF-based methods and supports the fabrication of complex geometries in emerging semiconductor, superconducting, and quantum technologies.

This work is carried out through a collaboration between Lawrence Berkeley National Laboratory, the Molecular Foundry, and the University of Copenhagen as part of the NQCP program, enabling coordinated development of low-temperature ALE for next-generation nano- and quantum device fabrication.

ALE-MoP-2 Active-Learning Accelerated Atomistic Modeling of ALE Processes, ***Fedor Goumans,*** Software for Chemistry & Materials, Netherlands; *Nestor Aguirre,* Softare for Chemistry & Materials, Netherlands; *Nicolas Onofrio,* Software for Chemistry & Materials, Netherlands

Atomic-layer etching (ALE) demands recipe windows that remove target material while avoiding interface damage. We introduce an ML-augmented multiscale modeling pipeline for ALE that combines DFT energetics, an active-learning machine learning interatomic potential (MLIP), automated reaction discovery, and 3D kinetic Monte Carlo (kMC) growth/etch simulations to predict spatial trap-density proxies and etch-selectivity maps. A task-adapted MLIP, fine-tuned from a small DFT seed set via uncertainty-guided sampling, accelerates PES exploration and identifies candidate dissociative and adsorption channels as well as penetration of the etchant or plasma ions. Only structure with high uncertainty in energies and forces are re-computed with DFT, limiting the DFT budget while ensuring accuracy for kinetically relevant steps. The final, DFT-verified reaction network drives 3D-kMC simulations that produce rasterized maps of (near-interface) defect proxies as a function of etchant kinetic energy, flux, and surface termination. We present two ALE case studies: Ru/H and SiO2/HF etching giving insights in how the processes (energies, fluxes) can affect the resulting structures and electronic properties of the etched thin films.

ALE-MoP-3 Stabilization of Etch Rate in SiO_2 Quasi-ALE Using an O_2 Plasma, ***Akimi Uchida,*** *Tomoyuki Nonaka, Koshi Hanada,* Samco Inc., Japan

Fluorine-based quasi-atomic layer etching (quasi-ALE) of SiO_2 is widely used as an ALE process. However, in this process, fluorocarbon (CF) polymers deposited on the reactor chamber re-evaporate and redeposit on the wafer surface, causing the etch rate per cycle to gradually increase with increasing cycle number [1,2]. This behavior originates from the fact that, unlike ideal ALE, the modification step in quasi-ALE does not proceed in a self-limiting manner, and the etch rate depends on the thickness of the deposited film. As a result, even when cycles are repeated under identical process conditions, the etch amount per cycle cannot be maintained at a constant value. In this study, we focus on the instability of the etch amount per cycle and propose a method to stabilize it. A SiO_2 quasi-ALE process using C_4F_8/Ar gas was employed, in which modification and removal steps were alternately repeated in a cyclic manner. To remove CF polymers deposited on the reaction chamber and stabilize the etch amount per cycle, a short O_2 plasma step (several seconds) was inserted after the removal step of each cycle. The etch amount per cycle was evaluated and compared with and without the O_2 plasma step.

Without the O_2 plasma step, the etch amount per cycle increased after approximately 50 cycles, leading to a loss of linearity in the etch rate. In contrast, when the O_2 plasma step was introduced in every cycle, the etch amount per cycle remained nearly constant throughout all cycles, resulting in stable linear etching characteristics. Furthermore, the self-limiting behavior observed during the removal step exhibited similar saturation characteristics regardless of the presence or absence of the O_2 plasma step.

These results demonstrate that the proposed method effectively stabilizes the etch amount per cycle in fluorine-based SiO_2 quasi-ALE processes by suppressing cycle-to-cycle variations without altering the underlying reaction mechanism.

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ALE-MoP-4 Ion-beam Atomic Layer Etching for Effective Damage Removal in Vertical GaN-Based Devices, ***Sung Hyun Kim***, *Jong Soon Park, Geun Young Yeom,* Sungkyunkwan University (SKKU), Republic of Korea

GaN is a wide-bandgap semiconductor that exhibits excellent electrical and optical properties, making it suitable for LED device. In particular, it is well-suited for light-emitting diodes due to its direct bandgap property. [1] Light-emitting devices adopt a mesa structure to expose multi-quantum well (MQW) layer composed of InGaN and GaN emitting layer. A direct plasma-based etching process is commonly used to form these structures. [2] Unfortunately, reactive ions accelerated by the combined potential of the self-bias and sheath inevitably induce structural and physical damage, which particularly lead to electrical and optical degradation of the MQW. To mitigate plasma-induced damage, wet etching techniques using KOH solutions are employed to remove the damaged GaN surface layer. [3] Subsequently, atomic layer etching (ALE) has been investigated to eliminate the remaining damage layer. However, ALE conducted in direct plasma cannot efficiently target vertical GaN structures including MQWs, because accelerated ions are incident perpendicularly to the surface. To address this issue, ALE utilizing an ion-beam source has been investigated, enabling selective targeting of MQW layers through the use of tilted ion beams.

In this study, atomic layer etching (ALE) utilizing an ion beam is introduced after RIE process to remove the damage caused by RIE in GaN-based structures, including multi-quantum well (MQW) layers composed of InGaN and GaN. X-ray photoelectron spectroscopy (XPS) analysis reveals that RIE-induced damage alters the N/Ga and Ga/In atomic ratios relative to reference data. However, after ion-beam ALE treatment following RIE, the atomic ratios return to values similar to the reference data, whereas wet etching only partially restores the atomic ratios. Consequently, ion-beam ALE is a promising approach for enhancing device performance by providing efficient surface damage removal, particularly in nanoscale vertical GaN-based devices.

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ALE-MoP-5 Highly Selective Atomic Layer Etching of Mo using O_2/Cl_2 by Formation of MoO_xCl_y, ***Su Jeong Yang***, *Yun Jong Jang, Geun Young Yeom,* Sungkyunkwan University (SKKU), Republic of Korea

As demand for high-performance chips increases, not only the critical dimension (CD) of device gates but also the CD of interconnect metals is decreasing. Cu is currently used as an interconnect material with a barrier material in a damascene structure because of low resistivity. However, there is a limit in scaling down of Cu width due to the existence of barrier metal, the need for new materials to replace Cu is increasing to overcome this limitation. Molybdenum (Mo) is one of the candidates for next-generation interconnect materials, as it has lower apparent resistivity (electron mean free path × bulk resistivity; $\lambda \times \rho_0$) than Cu when the critical dimension (CD) is below 10 nm.

In this study, anisotropic atomic layer etching (ALE) of Mo was performed using O_2 and Cl_2 plasma radicals as adsorption gases to precisely control the etch depth of Mo. The etch depth per cycle (EPC) of Mo and hard mask materials such as TiN, Si_3N_4 were compared in the Mo ALE process under Cl_2 and Cl_2:O_2 conditions. The results showed that, by adding O_2 to Cl_2, even though the Mo EPC is slightly decreased, highly selective Mo etching relative to TiN could be achieved. X-ray photoelectron spectroscopy (XPS) showed the formation of volatile MoO_xCl_y on the Mo surface during ALE which can be easily removed during the desorption step.

ALE-MoP-6 Improving Optical Resonator Quality Factors in Thin-Film Lithium Niobate with Atomic Layer Etching, ***Ivy Chen***, *Selina Zhou, Alireza Marandi, Austin Minnich,* California Institute of Technology

Thin-film lithium niobate (TFLN) is a nonlinear optical integrated photonics platform of intense interest, owing to its ability to generate and manipulate electromagnetic waves from a broad range of frequencies. Currently, the performance of on-chip devices based on TFLN is limited by imperfections arising from the fabrication process. Much of these imperfections originate from the dry etch process of lithium niobate, such as sidewall surface roughness, aspect ratio dependent etching, and other geometry inhomogeneities over the chip. Atomic layer etching (ALE) could be used to overcome these difficulties and enable unprecedented device performance. Recently, we have reported isotropic and directional HBr-based ALE processes that are able to smooth sidewalls (in the isotropic case) and achieve aspect ratio independent etching (in the directional case). Here, we present results on applying our isotropic and directional ALE processes to TFLN devices, along with other post processing methods, to improve the quality factor of optical resonators. The effect of ALE and subsequent processing on the surface roughness, sidewall surface roughness, and sidewall angle of TFLN devices will also be discussed. Using isotropic and directional ALE together to smooth sidewalls and achieve aspect ratio independent etching could enable unprecedented device performance and large-scale integration of photonic circuits.

ALE-MoP-7 Recovery of Plasma-Induced Surface Damage in Gan-Based Led via Atomic Layer Etching, ***Young Woo Jeon***, *Jong Woo Hong, Geun Young Yeom,* Sungkyunkwan University, Republic of Korea

Gallium Nitride (GaN)-based devices have emerged as key components in optoelectronic and power applications because their wide direct bandgap and high energy conversion efficiency enable superior performance. Light-emitting diodes (LEDs) and power semiconductors, in particular, strongly benefit from these material properties [1]. As the critical dimensions of LED structures continue to scale down, reactive ion etching (RIE) has been widely adopted to form anisotropic profiles during device fabrication. Nevertheless, energetic ion bombardment during the RIE process introduces surface and lattice damage, which degrades both the electrical and optical characteristics of GaN devices. Conventionally, wet etching has been employed as a post-treatment to mitigate this damage; however, its effectiveness is often limited by insufficient damage removal and residual surface defects [2–3].

To address this issue, atomic layer etching (ALE) was employed as a post-RIE treatment to selectively eliminate the damaged surface region in GaN-based structures, including InGaN/GaN multi-quantum well (MQW) layers. Transmission electron microscopy (TEM) images revealed that the MQW layers became indistinct after RIE, indicating structural deterioration. Although subsequent wet etching partially restored the layer contrast, TEM images showed that ALE produced much clearer interfaces, demonstrating more effective damage removal.Photoluminescence (PL) measurements indicated that RIE-induced damage increased as device dimensions decreased, but after the ALE, PL intensity was improved after ALE and became more significantly improved for smaller devices.Overall, as GaN-based LEDs continue to shrink in size, an efficient damage-recovery process becomes increasingly important. Compared with conventional wet etching, ALE offers superior surface restoration and is therefore a more suitable approach for enhancing device performance.

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ALE-MoP-8 Development Atomic Layer Etching of Ga_2O_3 Using CF_4 Plasma and $Sn(acac)_2$, *To-En Hsu, Yu-Hsuan Yu,* ***Chien-Wei Chen***, National Center for Instrumentation Research, National Institutes of Applied Research, Taiwan

Gallium oxide (Ga_2O_3), featuring an ultra-wide bandgap and a high breakdown electric field, is regarded as a promising material for high-power semiconductor devices; however, its etching process remains challenging in terms of achieving both high precision and low plasma-induced damage. Atomic layer etching (ALE), which employs cyclic self-limiting surface reactions, provides a potential solution for realizing highly controlled and low-damage etching.

In this study, a plasma-based ALE process for Ga_2O_3 using tetrafluoromethane (CF_4) plasma and tin(II) acetylacetonate ($Sn(acac)_2$) as sequential reactants is developed. The CF_4 plasma half-reaction is first investigated to verify the surface fluorination behavior of Ga_2O_3. The CF_4 plasma is operated at a power of 30 W and a working pressure of 0.5 Torr, with a reaction time of 5 s per cycle. A total of 5 cycles (25 s) and 25 cycles

(120 s) are performed to examine the evolution of surface chemical states. X-ray photoelectron spectroscopy (XPS) analysis reveals that the fluorine concentration on the surface increases with the number of plasma cycles (Figure 1). Meanwhile, the intensities of Ga and O signals decrease, indicating a signal attenuation effect caused by the formation of a fluorinated surface layer, which confirms effective surface fluorination of Ga_2O_3 by the CF_4 plasma. After confirming the surface fluorination behavior, $Sn(acac)_2$ is introduced as the second reactant to complete the full ALE process. During the full reaction cycles, the CF_4 plasma is applied at a power of 50 W with a reaction time of 10 s per cycle, while the process temperature is maintained at 450 °C. The $Sn(acac)_2$ exposure consists of a 0.1 s pulse followed by a 1 s soak, enabling the conversion of surface fluorides into volatile reaction products and their subsequent removal, thereby completing a single ALE cycle. Following the full ALE process, spectroscopic ellipsometry measurements show a continuous decrease in film thickness with increasing ALE cycle numbers, confirming effective atomic layer etching achieved by the combined CF_4 plasma and $Sn(acac)_2$ reactions (Figure 2). The average etching rate is approximately 0.105 nm per cycle.

Overall, this work demonstrates a repeatable and precisely controllable plasma-enhanced ALE process for Ga_2O_3, highlighting its potential for applications in ultra-wide bandgap semiconductor devices and advanced manufacturing technologies.

ALE-MoP-9 Thermal Atomic Layer Etching of Yttrium-Doped Hafnium Oxide Using Hydrofluoric Acid and Boron Trichloride, ***Aziz Abdulagatov***, *Andrew Cavanagh,* University of Colorado Boulder*; Florian Wunderwald, Uwe Schroeder,* NaMLab gGmbH, Germany*; Steven George,* University of Colorado Boulder

Y-doped HfO_2 (Y:HfO_2) is known to stabilize the orthorhombic/tetragonal (o/t) ferroelectric phase of HfO_2 and widen the ferroelectric thickness window. However, Y-doping in HfO_2 could also affect the thermal ALE of Y:HfO_2. In this study, Y:HfO_2 was etched using sequential exposures of hydrogen fluoride (HF) and boron trichloride (BCl_3). The initial Y:HfO_2 films with thicknesses of 10 nm were deposited on 10 nm of TiN with an underlying W layer of 30 nm. The Y:HfO_2 film thicknesses were then monitored during thermal ALE using in situ spectroscopic ellipsometry (SE) measurements.

The in situ SE measurements showed that sequential HF and BCl_3 exposures at 270 °C resulted in the linear decrease of the Y:HfO_2 thickness. The etch rate was 0.22 Å/cycle during the first 80 ALE cycles. Subsequently, there was a gradual reduction of the etch rate to ~0.15 Å/cycle over the next 60 ALE cycles (Figure 1). X-ray photoelectron spectroscopy (XPS) analysis before and after ALE showed an increase in the Y concentration from ~2 to 4 at.%. This increased Y concentration indicated preferential Hf removal during the ALE cycles. The reduced etch rate was attributed to the gradual Y accumulation on the surface. The Y buildup was consistent with thermochemical calculations that showed low favorability for BCl_3 ligand exchange with YF_3. $YF_3 + 2BCl_3(g) \rightarrow BF_3(g) + YCl_3(g)$ has an unfavorable ΔG(270 °C) = +41.1 kcal. In contrast, $HfF_4 + 4/3BCl_3(g) \rightarrow 4/3BF_3(g) + HfCl_4(g)$ has a favorable ΔG(270 °C) = −10.9 kcal.

Atomic force microscopy (AFM) measurements revealed only a minor increase in root-mean-square (RMS) roughness. The initial RMS roughness was 7.0 Å. The RMS roughness increased to only 7.7 Å after removal of 3 nm by etching. Grazing-incidence X-ray diffraction (GIXRD) analysis of the initial 10 nm Y:HfO_2 film showed only metastable o/t phases. After etching removal of 3 nm, GIXRD revealed no phase transformation and reduced peak intensity and peak broadening consistent with decreased crystallite size. In contrast, HZO ALE of a 10 nm HZO film thickness using HF and dimethylaluminum chloride (DMAC) showed transformation from predominantly o/t-phase to monoclinic phase after etching at 250 °C.

ALE-MoP-10 Thermal Gas-Phase Etching of Silicon Materials by Chlorination Using $SOCl_2$, SO_2Cl_2, and HCl, ***Troy Colleran,*** University of Colorado at Boulder

Silicon materials such as Si, Si_3N_4, SiO_2, and SiC play a critical role in the semiconductor industry. Selective etching of silicon materials while leaving nearby dielectric materials such as HfO_2 or ZrO_2 intact is a challenge in semiconductor device fabrication. In this study, the thermal etching of silicon materials by chlorination using $SOCl_2$, SO_2Cl_2, and HCl was explored using quadrupole mass spectrometry (QMS) studies on powders. The measure of etching was the appearance of SiCl4+ ion intensity during the QMS studies. Temperature ramp studies were performed to determine the onset temperature of each etching reaction.

The thermochemistry of etching silicon materials by $SOCl_2$, SO_2Cl_2, and HCl to produce $SiCl_4$ is favorable. However, reaction kinetics may dictate the feasible etching temperatures. Si chemical vapor etching (CVE) was demonstrated using $SOCl_2$, SO_2Cl_2, and HCl exposures above 200°C (Figures 1 & 2). SiO_2 CVE was achieved using SOCl2 exposure above 400°C. Si_3N_4 CVE was observed for $SOCl_2$, SO_2Cl_2, and HCl exposures above 200°C (Figure 3). SiC CVE was demonstrated for HCl exposures above 200°C (Figure 4). The SiCl4+ ion signal increased progressively at higher temperatures above the threshold temperature for all silicon materials. In contrast, there is selectivity for etching these silicon materials compared with HfO2 and ZrO2. Thermochemical calculations suggest that SO_2Cl_2 and HCl will not chlorinate either HfO_2 or ZrO_2. Etching HfO_2 and ZrO_2 using $SOCl_2$ requires temperatures above 350°C.

Etching of silicon materials by $SOCl_2$, SO_2Cl_2, and HCl required the removal of the native oxide on the initial silicon-containing powders prior to exposure to the chlorination precursors. The native oxide was removed by a 5 minute exposure to HF at 400°C. Time-resolved QMS data showed the evolution of H_2O+ and SiF_4+ ion signals during SiO_2 removal. The H_2O+ ion signal decreased during the HF exposure consistent with the native oxide removal. Si, SiC, and Si_3N_4 powders that were not treated with this initial HF exposure did not produce any $SiCl_4$+ ion signals during the $SOCl_2$, SO_2Cl2, or HCl exposure.

ALE-MoP-11 Atomic Layer Etching of Metal Oxides Using Halogen-Free Liquid Phase Organic Etchants, ***Hana Kim**, Hyeon Sik Cho, Hyun Ju Jung, Myeong Il Kim, Jaemin Kim, Duck Hyeon Seo, Juhwan Jeong, Sun Young Baik, Kyuho Cho,* EGTM Co. R&D Center, Republic of Korea

Atomic layer etching (ALE) of metal oxide thin films is of increasing importance for advanced device fabrication requiring precise thickness control and minimized surface damage. Most reported metal oxide ALE processes rely on halogen-based chemistries and, in many cases, metal-containing etchants to enhance surface reactivity [1-4]. In this work, we report a halogen- and metal-free ALE process for metal oxides enabled by halogen-free liquid phase organic etchants.

The ALE cycle consists of an etching step employing fully organic etchants followed by a reactive removal step that regenerates the surface for subsequent cycles (Fig. 1). The organic etching chemistry exhibits a clear saturation behavior with respect to etchant feed time, resulting in a self-limited etch-per-cycle (EPC) governed by etch-stop formation through surface reaction saturation. During sequential Etchant/Remover ALE, the etched thickness per cycle remains constant once the etchant feed time exceeds a critical window, demonstrating feed-time-limited material removal by the organic etchant (Fig. 2). This saturation behavior was consistently observed for both TiO_2 and Nb_2O_5 thin films.

In addition, a linear reduction in film thickness with increasing ALE cycle number was observed for TiO_2 thin films, demonstrating cycle-by-cycle controllability of material removal (Fig. 3). Similar linear etch behavior is being evaluated for Nb_2O_5 thin films under the same ALE scheme. The reactive removal step oxidatively eliminates or transforms etch-inhibiting surface species formed during the etch step; within the tested process window, the film thickness change is insensitive to the removal-step feed time, indicating that material removal is defined by the etch step rather than the regeneration step.

Unlike many reported metal oxide ALE processes that rely on halogen chemistry and/or metal-containing etchants to enhance reactivity, the present approach achieves self-limited etching through organic reaction saturation and reactive surface regeneration alone. These results demonstrate a halogen- and metal-free ALE approach for metal oxides based on organic reaction saturation, providing a controllable and damage-mitigated etching method for functional oxide materials.

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ALE-MoP-12 Reaction Mechanism of Isotropic Atomic Layer Etching of Zirconium Oxide: An *In Vacuo* X-ray Photoelectron Spectroscopy Study, ***Hye-Lee Kim**, Mi-Soo Kim, Eunju Ham, Sejeong Jo, Hyun-Jeong Yoo,* Sejong University, Republic of Korea*; Youn Seoung Lee,* Hanbat National University, Republic of Korea*; Sun-Jae Kim, Won-Jun Lee,* Sejong University, Republic of Korea

The advent of complex 3D semiconductor architectures, such as gate-all-around (GAA) field-effect transistors (FETs) and vertical memory structures,

has increased demand for isotropic atomic layer etching (ALE) to achieve precise, damage-free patterning. The ALE process typically relies on a self-limiting cycle comprising a surface modification step followed by a subsequent removal step. However, a fundamental understanding of these half-reactions is often obscured by surface oxidation and adventitious carbon contamination that arise during air-exposed sample transfer for ex situ analysis. In this study, we present an investigation of ZrO_2 isotropic ALE using a custom-built in vacuo X-ray photoelectron spectroscopy (XPS) system. By integrating the ALE process chamber directly with the XPS analysis chamber under high vacuum, we successfully characterized the surface chemical states of each half-reaction without atmospheric artifacts. Our *in vacuo* analysis revealed distinct surface evolution during the ALE cycles that were unobservable in conventional *ex situ* measurements. During the modification step using NF_3 remote plasma, Zr–O bonds were converted to Zr–F bonds, confirming effective surface fluorination. In the subsequent removal step using dimethylaluminum chloride (DMAC), the depletion of the Zr–F signal was accompanied by the appearance of specific ligand residues derived from DMAC. This step-by-step tracking enabled us to confirm the reaction pathways via ligand exchange. Notably, the *in vacuo* capability enabled high-sensitivity detection of trace surface residues that would have been indistinguishable in ex situ analysis due to the air exposure. These findings are critical for optimizing isotropic ALE processes for next-generation high-k dielectric applications.

ALE-MoP-13 Numerical and Experimental Investigations on Tailored Waveforms, ***Sebastian Mohr**, Hyungseon Song,* Quantemol Ltd., UK*; Ben Harris, Daryl White, Geoff Hassall,* Oxford Instruments Plasma Technology, UK*; James Ellis,* Oxford Instruments, UK

Atomic layer etching (ALE) is increasingly used in the manufacturing of semiconductor tools as it enables more control over the resulting etching profiles than traditional etching techniques. While different approaches to ALE exist, many of them employ plasmas in one or more steps of the ALE process, be it to use the neutral radicals produced in the plasma to alter the surface or the ions to remove the altered top layer [1].

For such applications, independent control of ion flux and ion energy is highly desirable. Single frequency capacitively coupled discharges (CCPs) do not offer this, as the input power affects both flux and energy. Dual frequency discharges allow this to some extent, but it is limited due to, for example, increased ionization by secondary electrons at high powers of the low frequency. Furthermore, traditional CCPs usually produce bimodal ion energy distribution functions which can cover several 10s to 100s of eV with sharp peaks at either end, so the ion energy cannot be easily limited to a small interval of energies, which is desirable especially for ALE applications, so that the ions remove the top layer of the surface but do not damage the underlying bulk [1].

An alternative approach to achieve this desired control are tailored waveforms. These can range from so-called asymmetric waveforms combining a fundamental frequency with even multiples [2] to non-sinusoidal waveforms typically consisting of sharp voltage peaks [1] followed by a relatively long interval of an almost constant voltage. While it has been demonstrated that these types of CCPs offer independent control of ion flux and energy and/or are able to limit the ion energy to narrow energy intervals, they have not yet been well studied in industrial applications.

This presentation will show our continued efforts to simulate industrial applications of ICPs combined with tailored waveforms to allow precise control of ion energies. The simulations are carried out with the Hybrid Plasma Equipment Model [3]. The simulated results are compared to experimental results with a focus on how the precise shape of the tailored waveform affects the ion energy distribution measured at the electrode for different pressures and ICP powers.

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ALE-MoP-14 Thermal Etch and SEM3D–Modeling Driven Profile Engineering for Metal–Gate Corner Preservation in Advanced MEOL SAC Processing, ***Prabhat Kumar**,* Lam Research Corporation

As middle–of–line (MEOL) scaling advances, robust source–drain (S/D) contact formation—especially in self–aligned contact (SAC) schemes—has become critical to device performance, yield, reliability, and power efficiency. At aggressively scaled nodes, small deviations in contact geometry can significantly increase resistance and leakage. A major challenge in current plasma–based etch processes is **metal–gate corner loss**, which degrades gate integrity and is expected to worsen with further CD shrink.

To address this, we developed an **innovative thermal etch process** capable of minimizing corner loss while achieving high metal gate selectivity. The method utilizes liquid precursor and HF gas delivered under vacuum in cyclical or co–flow operation. Liquid is vaporized through a heated delivery system, while HF is introduced through the gas manifold; these species react in situ to form a neutral–dominant, chemical etch pathway that selectively removes oxide without physically damaging metal gates. This enables highly selective oxide etching while preserving the sensitive gate corners that are typically eroded in ion–driven plasma processes.

Because thermal etching relies predominantly on neutral–chemistry reactions rather than directional ions, controlling the lateral component of the etch and maintaining profile fidelity are key challenges. To overcome this, we introduced a **conformal liner deposition step**, which shapes the sidewalls prior to thermal etch, followed by a **breakthrough process** that removes polymer at the etch front to enable clean thermal–oxide removal. This hybrid approach stabilizes the feature profile, suppresses lateral encroachment, and significantly reduces corner retreat.

To optimize process behavior and quantify the impact of neutral–driven reactions, we modeled the thermal etch using the **SEMulator3D (SEM3D)** profile simulator. SEM3D was calibrated to wafer data and used to capture lateral–etch tendencies, reaction penetration depth, and sensitivity to liner thickness and thermal–etch conditions. Modeling results guided the development of a combined **liner + thermal etch sequence** that minimizes lateral loss, improves uniformity, and preserves gate–corner geometry. The SEM3D–based DOE accelerated tuning of precursor flow, sticking behavior, cycle time, and breakthrough parameters, enabling precise control of the etch front.

Across customer wafers and device test structures, the integrated process demonstrated **excellent metal–gate selectivity**, near–elimination of corner loss, and strong compatibility with existing MEOL integration schemes. By coupling a novel thermal etch chemistry with physics–based profile modeling and a liner–assisted control strategy, this work provides a scalable and manufacturable solution to one of the most critical challenges in future SAC–based S/D contact formation.

ALE-MoP-15 Modelling Atomic Layer Etching of a ZnO Surface Using Thermogravimetric Analysis and Solvothermal Synthetic Methods, ***Justin Moore**, Titel Jurca,* University of Central Florida

Atomic layer deposition (ALD) is the backbone of the modern semiconductor industry, allowing for the deposition of films with atomic scale control for the creation of sub 5 nm nodes. Atomic layer etching (ALE), a relatively more recent process, has proven itself to be just as essential as its ALD counterpart, allowing for the removal of material with atomic scale precision. Despite this, ALE lacks the diversity of precursors afforded to ALD processes due in part to the challenge of modifying a surface while also ensuring the resulting reaction products are volatile and thermally stable enough to be removed cleanly. Herein we demonstrate a method to model and isolate the products of an ALE process, encompassing ZnO and a series of acetylacetonate precursors, utilizing thermogravimetric analysis (TGA) and small scale solvothermal reactions (synthesis).

Acetylacetone precursors with more electron withdrawing functionalities exhibit increased reactivity with ZnO, while acetylacetone precursors with more electron donating functionalities exhibit reduced to no reactivity with ZnO. Isolation and subsequent TGA analysis of the resulting zinc acetylacetonate complexes reveal that more fluorinated complexes are more volatile at temperatures relevant for an ALE process. This approach demonstrates a fast and efficient process to screen precursors that could effectively etch a surface to yield volatile thermally stable byproducts. This bypasses the need for an ALD/ALE reactor in the preliminary studies, and as a result expedites the discovery phase while lowering the associated costs and efforts around ALE process optimization.

ALE-MoP-16 Exploring Hydrofluorocarbons for Thermal ALE of High-k Oxides, ***Michael Nolan**,* Tyndall Institute, Ireland*; Rita Mullins,* Tyndall National Institute, University College Cork, Ireland

Thermal Atomic Layer Etching (ALE) has potential to deliver atomic level control over the etch of many materials and in particular for future CMOS nodes with requirements for sub-nm levels of control on complex 3D structures. It is performed using sequential surface modification followed by reaction with a second precursor to release volatile products. The self-limiting surface chemistry typical for ALD is also exploited here with the modification and therefore etch limited to only the outer surface layer. For

metal oxides, typically HF is used to fluorinate the initial surface to form metal-fluoride layer (M = metal) which undergoes ligand-exchange with a precursor such as TiCl4 or SiCl4, which volatilizes the modified layer. HF is a toxic and challenging to handle chemical and other fluorides used in etch, e.g. CF4, C4F8 and NF3 are PFAS or have high global warming potential (GWP). Hydrofluorocarbons such as CH3F or CH2F2 have GWPs < 100 and are not strictly PFAS, lacking the terminal CF3 group. In this contribution we present first principles simulations of the potential for CH3F and CH2F2 to be used as alternatives to HF for ALE of high-k oxides HfO2, ZrO2 and HfZrO4. Our thermodynamic calculations show that self-limiting ALE can be preferred at temperatures relevant for CMOS processing. Detailed analysis of the interaction at the oxide surfaces, in particular the activation barriers for C-F bond break and surface fluorination show that these molecules generally have high barriers to C-F dissociation limiting their usefulness, which is shown by computed process maps. On amorphous HfO2 and HfZrO4, the hydrofluorocarbons can show low barriers to C-F bond breaking which suggests they may be useful alternatives to HF for amorphous and ternary oxide ALE.

ALE-MoP-17 Halogen-Free ALE of Copper, *Persi Panariti, Asare Dua,* ***Adam Hock,*** Illinois Institute of Technology

Controlled ALE of metallic copper without surface modification has proven challenging, because copper surfaces are relatively chemically inert. But modifying the surface by oxidation (i.e., forming a CuOx surface layer) facilitates the etch step, which consists of removal of the modified layer as a volatile metal complex. Therefore, Cu oxidation is especially important for enabling ALE. We have developed a novel ALE process for Cu metal that is halogen-free and operates at temperatures less than 200°C. This poster describes our *in situ* characterization of the ALE mechanism and ALE results on Cu thin films.

ALD for Manufacturing
Room Tampa Bay Salons 5-9 - Session AM-MoP
ALD for Manufacturing Poster Session

AM-MoP-1 Implementing Statistical Process Control for Atomic Layer Deposition Tools in an Academic Facility to Meet Industrial Expectations, *Ronald Reger,* Birck Nanotechnology Center, Purdue University*;* ***Anh Ho,*** Birck Nanotechnology Center, Purdue University*.; Rich Hosler,* Birck Nanotechnology Center, Purdue University

As academic nanofabrication facilities expand their role in advanced research and prototype development, the demand for industrial-level process stability and repeatability in Atomic Layer Deposition (ALD) has become essential. At the Birck Nanotechnology Center, we have implemented a comprehensive Statistical Process Control (SPC) framework applied to multiple Fiji ALD systems to enhance process reliability. The key metrics, including film thickness, uniformity, growth-rate, refractive index, surface roughness, precursor delivery stability, and overall tool-health indicators, were continuously tracked using control charts, capability analyses, and automated data-logging integrated into routine operations. Over several years, SPC-driven maintenance strategies, precursor delivery stability, and recipe standardization have enabled improvements in within-wafer and wafer-to-wafer uniformity, reduced run-to-run variability, and enhanced long-term reproducibility. Several dielectric ALD processes now demonstrate statistically stable performance with sustained operation within established control limits. This work not only demonstrates the value and practicality of applying formal SPC methodologies within an academic cleanroom, effectively bridging research-grade flexibility with industry-grade reliability, but also contributes significantly to building the data foundation for a digital twin model for educational purposes. The results offer a model for academic facilities aiming to improve tool performance, build user confidence, and meet industry-aligned research expectations.

AM-MoP-2 Anti-Deposition ALD–Al_2O_3 Coatings against Silicon Chloride Byproduct for Capacitance Manometers, ***Hidenobu Tochigi,*** *Keigo Iwamoto, Takuya Ishihara,* Azbil corporation, Japan

In semiconductor manufacturing processes such as dry etching and thin–film deposition, including chemical vapor deposition (CVD) and atomic layer deposition (ALD), capacitance manometers are widely used as essential vacuum pressure sensors to monitor and control the pressures of process gases. Conventionally, diaphragm materials such as nickel-based alloys and polycrystalline aluminum oxide (Al_2O_3) are employed to ensure durability under chemically harsh environments. Sapphire, a single crystal of Al_2O_3, is known for its excellent chemical stability, and we have developed MEMS-based pressure sensor chips entirely fabricated from sapphire [1]. In actual application, long-term drift and zero-point shift of the sensors have been observed during semiconductor manufacturing processes, which are presumed to be caused by byproduct deposition on the sensor surfaces.

In particular, processes using silicon-chloride precursors are known to generate chlorine–containing reactive intermediates and byproducts that can potentially deposit on the sensor surfaces. Previous studies on ALD processes have reported that a self–limiting surface reaction mechanism, in which SiCl–containing precursors selectively react with reactive surface functional groups such as –OH and –NH, and further adsorption is suppressed once these reactive sites are consumed [2-5]. Based on this concept, we hypothesized that similar self–limiting reactions could occur on –OH–terminated Al_2O_3 surfaces deposited by ALD and could consequently suppress the continuous formation of SiCl–related deposits on the sensor surfaces. If effective, this mechanism could be applied as a byproduct deposition mitigation strategy for capacitance manometers used in similar processes.

To verify this hypothesis, Al_2O_3 coatings were deposited by ALD using trimethylaluminum and H_2O over the entire internal surfaces of capacitance manometers, and their behavior under SiCl–based process environments was evaluated. As a result, the ALD–coated manometers showed no such degradation, whereas uncoated manometers exhibited zero–point shifts of approximately 40% of full scale and pronounced pressure hysteresis, which exhibited excellent an anti-deposition effect. In addition, the deposited Al_2O_3 film quality was examined in detail by X–ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM).

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AM-MoP-3 Enabling Vacuum Process Monitoring with Time-of-Flight Spectroscopy, *Klaus Bergner, Marco John, Andreas Trützschler,* VACOM, Germany*;* ***Christopher Gray,*** VACOM, Belgium

The increasing complexity of industrial vacuum processes requires broader and deeper knowledge of the vacuum itself. A crucial aspect for increasing quality demands is the necessity of in-situ monitoring and control of pressure and residual gas composition within vacuum processes. A consequence of advanced process control is the reduction of production errors, prevention of failures or major damage in combination with increased operating time. Traditional monitoring devices like hot cathodes or quadrupole mass spectrometers are both only able to measure either pressure or residual gas composition. Therefore, these devices are only conditionally suited for complete process control of vacuum processes. With our novel wide-range vacuum monitor NOVION® industrially available pressure and gas analyzation is possible.

In this talk we present the fundamental principles of the novel vacuum monitor and explain the compact combination of well-known time-of-flight spectroscopy with our own patented ion trap. Within different application cases we discuss advantages and limits of this technology and demonstrate with one single device wide range gas analysis, simultaneous measurement of total and partial pressures, leak detection for Helium and detection of air leaks. With these combined capabilities the novel vacuum monitor is able to quickly capture the complete pressure and gas composition measurement at various stages of the vacuum process chain.

AM-MoP-4 Additively Manufactured Silicon Carbide Process Components Enabling Stable ALD/ALE Under Harsh Semiconductor Manufacturing Environments, ***Youngsuk Jung,*** *Ji-Won Oh, Shinhu Cho,* MADDE, Republic of Korea

Silicon carbide (SiC) has been widely adopted as a chamber material for advanced semiconductor manufacturing due to its excellent thermal stability, chemical resistance, and plasma durability. However, as atomic layer deposition (ALD) and atomic layer etching (ALE) processes continue to evolve toward higher aspect ratio features, plasma-enhanced conditions, and extended process runtimes, conventional manufacturing routes for SiC components increasingly limit achievable performance, particularly in terms of thermal uniformity, weight reduction, and geometric flexibility.

In this work, we focus on the advantages of additively manufactured SiC process components as a next-generation hardware solution for stable ALD

and ALE operation. Additive manufacturing enables design-for-additive-manufacturing (DfAM) approaches that allow the realization of customized, complex internal structures such as optimized gas flow channels, lattice-supported geometries, and locally tailored wall thicknesses. These design freedoms directly address key performance requirements in ALD/ALE chambers, including improved temperature uniformity, reduced thermal mass, and lightweight structures that facilitate faster thermal response and improved process controllability.

The presented SiC components are fabricated using a proprietary SiC-dedicated additive manufacturing platform, followed by a fully integrated post-processing route that includes densification and chemical vapor deposition (CVD) SiC coating. This end-to-end manufacturing capability, spanning from DfAM to final surface engineering, enables precise control over both bulk geometry and surface properties critical for plasma-facing and chemically aggressive ALD/ALE environments.

The interaction of additively manufactured and CVD-coated SiC components with representative ALD/ALE process conditions is discussed with an emphasis on structural integrity, contamination behavior, and long-term stability under repeated thermal and plasma cycling. The results demonstrate that additively manufactured SiC hardware provides a practical pathway to performance optimization beyond what is achievable with conventionally manufactured SiC components, highlighting its potential role in next-generation ALD and ALE manufacturing platforms.

Emerging Materials and Processes
Room Tampa Bay Salons 5-9 - Session EM-MoP
Emerging Materials and Processes Poster Session

EM-MoP-1 Chromium-Doped ALD Lead Telluride Thin Films with Additional Iodine Coating, ***Haifeng Cong***, *Helmut Baumgart,* Old Dominion University*; Tarek Abdel-Fattah,* Christopher Newport University

Thermoelectric materials directly convert heat into electricity, and PbTe is a promising narrow bandgap material due to its high Seebeck coefficient, chemical stability, and ability to operate at elevated temperatures (600–850 K). While PbTe thin films deposited by Atomic Layer Deposition (ALD) have been widely studied, doping thin films to enhance their thermoelectric performance remains less explored.In this study, PbTe thin films were synthesized on silicon substrates with native oxide via ALD using Pb(II)bis(2,2,6,6-tetramethyl-3,5-heptanedionato) and (trimethylsilyl) telluride as precursors. Chromium (Cr) was incorporated into the ALD films to modify electrical properties. An additional surface modification was performed by coating the PbTe:Cr films with iodine, followed by thermal treatment in a furnace at 80 °C for 72 hours, producing films with implanted Cr^{+} and iodine.Comprehensive characterization included X-ray diffraction (XRD) for crystal structure, FE-SEM for morphology, AFM for surface roughness, EDS and XPS for elemental composition and chemical states, and measurements of Seebeck coefficient, Hall effect, and thermal conductivity. Comparative analysis was conducted between Cr-doped PbTe films without iodine top coating and those with the iodine-treated top layer. Results show that the iodine modification further influences the electrical properties and thermoelectric figure of merit (ZT), highlighting the potential of combined Cr doping and surface engineering for high-performance PbTe thin films.

EM-MoP-2 Formation of Multi-Heterojunctions via Atomic Layer Etching for High Performance MoS_2 Photodetectors, ***Si Yeon Kim***, *Sun Jae Jeong, Ji Eun Kang, Geun Young Yeom,* Sungkyunkwan University (SKKU), Republic of Korea

In this study, high performance 2D MoS_2 photodetectors incorporating multi-heterojunction structures were fabricated through Atomic Layer Etching (ALE). By precisely controlling the thickness of the MoS_2 thin films using an ALE technique, MoS_2 heterojunctions composed of monolayer and multilayer regions were successfully formed. This engineered bandgap modulation facilitated the generation and separation of photo-induced carriers, thereby significantly enhancing the device's photoresponsivity.

Furthermore, the formation of multi-junction interfaces increased the effective contact area with the electrodes, securing superior electrical characteristics. Unlike conventional approaches that rely on hybrid heterostructures, this work distinguishes itself by simultaneously optimizing electrical and optoelectronic performance within a single material platform. These results demonstrate that ALE is a scalable and effective technique for manipulating 2D materials, paving a new way for next-generation optoelectronic applications.

EM-MoP-3 Plasma-Assisted Defect Engineering of MoS_2 for Controlled N-Type Doping and Phase Transition, ***Ga-Hee Oh***, *Sun Jae Jeong, Ji Eun Kang, Geun Young Yeom,* Sungkyunkwan University (SKKU), Republic of Korea

Precise control of doping type and concentration in transition metal dichalcogenides (TMDs) is essential for realizing TMD-based electronic devices, including p-n diodes, field-effect transistors (FETs), and tunnel FETs. However, conventional ion implantation techniques are not suitable for two-dimensional materials due to severe lattice damage and structural degradation.

This study presents an approach for achieving controlled n-type doping and structural phase transition in CVD-grown MoS_2 through atomic-scale plasma-assisted defect engineering. Although radical-based surface doping is generally limited by shallow penetration depth, Argon plasma treatment was applied to the MoS_2 surface, creating sulfur vacancies that effectively introduced n-type doping characteristics. The density of these sulfur vacancies and thereby the doping concentration was precisely tuned by varying the plasma exposure duration.

In addition to doping, the defect formation induced a phase transformation from the semiconducting 2H phase to the metallic 1T phase. Raman spectroscopy confirmed the emergence of new peaks associated with the 1T phase. Raman spectroscopy confirmed the emergence of new peaks associated with the 1T phase, while X-ray photoelectron spectroscopy (XPS) provided evidence of both chemical and structural changes during the process. These plasma – induced modifications resulted in substantial improvements in device performance, such as increased field-effect mobility and higher on/off current ratios. The ability to simultaneously control both carrier type and structural phase makes this method particularly promising for the design of high-performance two-dimensional (2D) electronic devices.

Overall, the results demonstrate that plasma-assisted defect engineering offers a scalable and controllable pathway for tuning the electronic properties of 2D transition metal dichalcogenides like MoS_2. This technique opens new possibilities for the development of next-generation nanoelectronics and optoelectronic devices.

EM-MoP-4 Fabrication of p-type Al-doped SnO_x Thin Films via Supercycle ALD using Sn4+-based Precursor, ***Suhyeon Park***, *Jiseop Byeon, Minjae Kwon,* Kyungpook National University, Republic of Korea*; Roy Byung Kyu Chung,* Kyungpook National University

Tin oxide (SnO_x) is a promising material for oxide semiconductor devices, such as thin-film transistors (TFTs), due to its tunable electronic properties derived from the multivalent nature of Sn^{2+} and Sn^{4+}. While SnO_2 is a typical n-type semiconductor, SnO exhibits p-type conductivity [1], making it suitable as a complementary material in complementary metal oxide semiconductor (CMOS) circuits. However, SnO is thermodynamically unstable and easily oxidized, requiring precise stoichiometry control. [2, 3] Previous studies have attempted to realize p-type SnO using atomic layer deposition (ALD) processes with Sn^{2+}-based precursors. [4, 5, 6] However, these precursors often suffer from limited commercial availability or high costs, hindering their practical use in research. In contrast, ALD processes employing Sn^{4+}-based precursors tend to favor the formation of stable n-type SnO_2, making p-type conduction difficult to achieve. To overcome these limitations, Al doping was employed as a key strategy to realize p-type SnO_x thin films using Sn^{4+}-based precursors.In this work, p-type Al-doped SnO_x (Al-SnO_x) thin films were fabricated through a supercycle ALD process using Tetrakis(dimethylamino)tin(IV) (TDMASn) as a Sn^{4+}-based precursor and Trimethylaluminum (TMA) as an Al_2O_3 source. The influence of the Al concentration and the spatial insertion position of the Al layer within the supercycle was systematically investigated. The optimal electrical performance was achieved when the Al layer was positioned in the middle of the SnO_2 layers. At an optimized Al concentration of 1.22 at%, the films exhibited a Hall mobility of 1.42 $cm^2/V{\cdot}s$ and a carrier concentration of 2.35 $\times 10^{18}$ cm^{-3} after post-annealing in a forming gas atmosphere. To evaluate electrical and structural characteristics of the films, Hall effect measurements and Grazing Incidence X-ray Diffraction (GIXRD) were primarily performed.This study demonstrates the feasibility of forming p-type films using cost-effective precursors. The optimization of both Al content and its spatial distribution allowed for precise control over the film's electrical characteristics. Based on these optimized process conditions, the controlled integration of n-type SnO_2 and p-type SnO_x films is expected to contribute to the future realization of tin oxide-based CMOS technology.

EM-MoP-5 Molecular Layer Deposited Hf-Based Hybrid Photoresists for Dual-Tone EUV Lithography, ***Thi Thu Huong Chu**, Dan N. Le, Minki Choe, Dushyant M. Narayan, Minjong Lee, Soham Shirodkar,* University of Texas at Dallas*; Nikhil Tiwale, Chang-Yong Nam,* Brookhaven National Laboratory*; Jiyoung Kim,* University of Texas at Dallas

Hafnium-based hybrid photoresists have emerged as promising candidates for extreme ultraviolet (EUV) lithography due to their high EUV absorption, superior etch resistance, and potential for sub-10 nm patterning.[1,2] Beyond their conventional single-tone behavior, our studies have revealed that Hf-based inorganic–organic hybrid materials can exhibit dual-tone responses under EUV exposure, enabling both positive- and negative-tone patterning within the same resist platform. This unique capability opens new opportunities for process simplification and enhanced patterning flexibility in advanced lithographic applications.

In this work, we demonstrate dual-tone EUV patterning using Hf-based hybrid photoresists and systematically evaluate their lithographic performance under both EUV exposure and low-energy electron-beam lithography (100 V EBL). We show that the resist tone can be switched via post-deposition treatment, which induces chemical changes within the Hf-based resist and results in tone inversion from conventional negative to positive tone behavior. The Hf-based hybrid resist films were fabricated via molecular layer deposition (MLD) using TDMA-Hf as the inorganic precursor and 2,3-dimercapto-1-propanol (DMP) as the organic linker. The MLD-derived hybrid resist exhibits high sensitivity, with the critical doses of 17.6 and 18.5 mJ/cm^2 for negative- and positive-tone modes, respectively. The critical doses required for both negative- and positive-tone patterning are comparable, indicating minimal sensitivity penalty when switching between tone modes.

Mechanistic investigations were conducted using *in-situ* FTIR and XPS analysis. The results indicate that negative-tone behavior arises from exposure-induced crosslinking, which stabilizes the resist film after development. In contrast, post-treated films exhibit positive-tone behavior, where film hardening is followed by bond scission under EUV or e-beam exposure, leading to enhanced solubility in the developer.

These findings highlight the versatility of Hf-based hybrid photoresists as multifunctional EUV resist materials and underscore their potential for next-generation EUV lithography, where adaptable tone control and simplified process integration are increasingly critical.

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EM-MoP-6 Deterministic Resistive Switching via Atomic-Layer Control of 2D WS_2 and Confined Ag Electrodes, ***Sihoon Son**, Taesung Kim, Hyunbin Choi, Geonwook Kim,* Sungkyunkwan University (SKKU), Republic of Korea

Atomic-scale control of both the active switching medium and the ionic source is a critical requirement for achieving reliable and scalable resistive memory technologies. While two-dimensional (2D) materials offer an intrinsically thin and well-defined switching layer, resistive switching in filamentary memories is still dominated by stochastic variations originating from uncontrolled metal-ion supply. Here, we demonstrate a resistive memory platform in which the resistive switching behavior is deterministically governed by the simultaneous atomic-layer-level control of a 2D WS_2 switching medium and the confined supply of Ag ions, enabled by ALD/ALE-compatible thickness engineering.

The WS_2 switching layer was synthesized with atomic-scale thickness control, allowing systematic modulation of the vertical transport length and defect density. In parallel, the Ag electrode was intentionally confined in both thickness and areal distribution, limiting the total Ag reservoir available for electrochemical metallization. By independently tuning the WS_2 thickness and the Ag supply, we reveal a clear transition in resistive switching behavior from Ag-dominated metallic conduction to vacancy-mediated switching governed by sulfur-vacancy (V_s) percolation. Electrical measurements combined with thickness-dependent statistics show that the high-resistance state is primarily dictated by the WS_2 thickness, whereas excessive Ag supply leads to unstable low-resistance states and increased variability.

Detailed electrical analysis and finite-element simulations indicate that a partially formed Ag tip, generated under confined Ag conditions, produces a highly localized electric-field enhancement at the WS_2 interface. This localized field drives controlled V_s migration along grain boundaries without forming a continuous metallic filament. The resulting sequential switching process—comprising partial Ag filament formation, transient space-charge-limited conduction, and eventual vacancy filament percolation—yields sub-percent switching variability and stable non-volatile memory operation. Importantly, ex-situ structural and compositional analyses confirm the absence of residual Ag within the WS_2 layer after switching, highlighting the non-metallic nature of the final conductive pathway.

By demonstrating that resistive switching characteristics can be deterministically programmed through atomic-scale thickness control of a 2D switching medium and precise limitation of metal-ion supply, this work establishes a materials-level design strategy directly aligned with ALD/ALE processing. The presented approach provides a scalable pathway toward highly uniform RRAM and neuromorphic memory devices, in which variability is suppressed not by circuit-level compensation but by atomically engineered material interfaces.

EM-MoP-7 BEOL Compatible Direct Growth of MoS_2 for Cu free Hybrid Bonding, ***Hyunbin Choi**,* Department of Semiconductor Convergence Engineering, Sungkyunkwan University, Republic of Korea*; Sihoon Son,* SKKU Advanced Institute of Nanotechnology (SAINT), Sungkyunkwan University, Republic of Korea*; Geonwook Kim, Taesung Kim,* School of Mechanical Engineering, Sungkyunkwan University (SKKU), Republic of Korea

Hybrid bonding technology is emerging as an essential solution for advanced 3D semiconductor integration, enabling the simultaneous bonding of metals and dielectrics. However, conventional hybrid bonding suffers from copper (Cu) contamination during the O_2 plasma activation step required for hydroxyl (OH) group formation on dielectric surfaces such as SiCN. The harsh plasma conditions induce Cu sputtering and migration, causing chamber and substrate contamination that degrades process reliability over time.To address this issue, we introduce a contamination free hybrid bonding approach employing an ultrathin molybdenum disulfide (MoS_2) barrier layer. The MoS_2 film is formed through plasma-enhanced chemical vapor deposition (PECVD) sulfurization of a Mo layer at low temperature. This barrier effectively suppresses Cu sputtering during O_2 plasma processing, preventing metal induced contamination while maintaining plasma activation efficiency.Furthermore, the MoS_2 layer enables post bonding electrical connection via memristive switching. Upon voltage application across the Cu–MoS_2–Cu structure, Cu ions migrate through the MoS_2 and form conductive filaments, ensuring reliable electrical connectivity without damaging the bonding interface.This work demonstrates a novel, BEOL compatible, Cu contamination free hybrid bonding process that preserves device integrity and enables high yield 3D integration. The proposed method provides a practical route toward cleaner, more reliable, and scalable hybrid bonding for next generation heterogeneous semiconductor systems.

EM-MoP-8 Monolithic 3D Artificial Intelligence Hardware Using four-Tier Vertically Integrated IGZO-Based HZO Ferroelectric Transistors, ***Geonwook Kim**, Sihoon Son, Hyunbin Choi, Taesung kim,* Sungkyunkwan University (SKKU), Republic of Korea

The relentless demand for faster, smaller and more energy-efficient integrated circuits has pushed the semiconductor industry to the performance, power and area (PPA) wall, where interconnect delay and energy dissipation dominate system efficiency. While 2.5D and TSV-based 3D integration offer partial relief, they suffer from long interconnects, thermal hotspots and reliability concerns. Monolithic 3D integration (M3DI) provides a transformative TSV-free paradigm, enabling nanoscale vertical interconnects between front-end-of-line logic and back-end-of-line memory tiers, thereby maximizing PPA efficiency and reducing latency. Here we demonstrate monolithic 3D integration (M3DI) of oxide thin-film electronics, integrating amorphous IGZO field-effect transistors with ferroelectric HZO field-effect transistors in a vertically stacked 1T-1FeFET architecture. These oxide-based thin-film devices are fully BEOLcompatible and highly scalable, providing uniform threshold voltage and I_{on}/I_{off} distributions for logic operations, as well as stable ferroelectric switching with narrow variability for memory functions. The resulting M3DI arrays enable ultra-dense integration, reproducible operation, and low-latency performance within a compact footprint. Beyond binary switching, the M3DI 1T-1FeFET architecture exhibits synaptic functionalities, including multilevel nonvolatile memory, spike-timing-dependent plasticity, and excellent array-level uniformity—key attributes for neuromorphic and AI

hardware. This work establishes oxide-semiconductor-based M3DI as a promising platform for next-generation intelligent and energy-efficient computing systems beyond conventional CMOS and von Neumann architectures.

EM-MoP-9 Annealing-Induced Structural Evolution and Crystallization Behavior of $CuNb_2O_6$, *Deug Hyun Nam,* Korea institute of industrial Technology, Republic of Korea*; Chan Woong Na,* Korea Institute of industrial technology, Republic of Korea*;* ***Yoon Myung****,* Korea Institute of Industrial Technology, Republic of Korea

$CuNb_2O_6$ is an intrinsic p-type metal oxide semiconductor in which hole transport originates from copper-derived electronic states embedded within an orthogonal Cu–O–Nb octahedral framework. This structurally ordered lattice provides stable and directional charge transport pathways, rendering crystallinity control essential for optimizing functional performance.

Herein, $CuNb_2O_6$ powders were synthesized via a sol–gel route followed by systematic thermal annealing to regulate crystal formation. The annealing-induced evolution of crystal structure and electronic states was comprehensively investigated using X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). Distinct temperature-dependent crystallization regimes were identified, accompanied by progressive stabilization of the Cu^{2+} and Nb^{5+} electronic environments and enhanced lattice ordering.

These results elucidate the coupled structural and electronic evolution of orthogonal $CuNb_2O_6$ during thermal processing and establish a crystallization window for achieving phase-pure and electronically optimized materials.

EM-MoP-10 Bias-Modulated ALD of Zinc Oxide*, **Jessica Jones**,* Argonne National Laboratory, USA*; Shi Li,* Argonne National Laboratory*; Rajeev Assary, Jeffrey Elam,* Argonne National Laboratory, USA

Biasing substrates during atomic layer deposition (ALD) in gaining popularity as a method to alter the resulting film. This is hypothesized to alter precursor–surface interactions and provide a means to tune material properties. We performed zinc oxide (ZnO) ALD using diethylzinc (DEZ) and water on silicon with native oxide substrates at 150 °C in a sample holder designed to create a static electrical field by biasing one plate of a parallel plate capacitor during deposition. ZnO films prepared in an electric field/on a biased sample holder were thinner, changed relative crystalline composition, and contained more carbon compared to samples grown under identical conditions without bias. Density functional theory (DFT) calculations showed enhanced electron migration between dissociatively adsorbed DEZ molecules and the ZnO (002) facet with increasing force from an electric field at the substrate surface, which strengthens the electronic interactions between the surface and the adsorbate. These models offer a compelling explanation for the inhibited growth, changes in the crystallinity, and increased carbon content of films grown in an electric field/on biased plates.

EM-MoP-11 Plasma-Enhanced Atomic Layer Deposition of Ferroelectric Aluminum Nitride*, **Nicholas Strnad**,* US Army Research Laboratory*; Gilbert B. Rayner Jr., Noel O'Toole,* The Kurt J. Lesker Company*; Nastazia Moshirfatemi,* General Technical Services, LLC*; Daniel Drury, Brendan Hanrahan,* US Army Research Laboratory*; Glen Fox,* Fox Materials Consulting, LLC*; Jeffrey Pulskamp,* US Army Research Laboratory

Piezoelectric aluminum nitride (AlN) and doped-variant aluminum-scandium nitride ($Al_{(1-x)}Sc_xN$) thin films are commercially essential for RF filters for wireless communication and have additional applications as sensors for piezoelectric ultrasound transducers (PMUTs), and energy harvesters. Recently, there have been a flurry of reports of ferroelectric sputtered $Al_{(1-x)}Sc_xN$ since its published discovery by Fichtner in 2019. Ferroelectric $Al_{(1-x)}Sc_xN$ has enormous potential as a memory thin film due to its extremely large, switched polarization (>>100 $\mu C/cm^2$) and Curie temperature > 1000° C, making it suitable for operation in extreme environments. Despite this excitement, there are few reports showing ferroelectricity in nominally undoped aluminum nitride, typically deposited using sputtering, due to the large electric fields (>6 MV/cm) required for switching. Here, we show ferroelectric AlN thin films grown by plasma-enhanced atomic layer deposition (PEALD) grown using ultra-high purity conditions. This is the first demonstration of ferroelectric PEALD AlN and only the second report of any ferroelectric nitride grown by PEALD. The PEALD AlN thin films were deposited at a substrate temperature of 300° C and exhibit room-temperature ferroelectric switching which is enabled by their enormous breakdown fields > 9 MV/cm. Trimethylaluminum (TMA) and alternatively N_2 and N_2/H_2 plasmas were implemented as co-precursors. The PEALD AlN films exhibited the wurtzite phase and grew in the c-axis (0002)-orientation on {111}-oriented Pt bottom electrodes deposited on (001) silicon with a 500 nm-thick thermal oxide.

EM-MoP-12 Thermal Atomic Layer Deposition and Post-Deposition Annealing of Molybdenum Oxide and Sulfide Thin Films*, Wesley Jen, **Nolan Olaso**, Icelene Leong, Steven M. Hues, Elton Graugnard,* Micron School of Materials Science and Engineering, Boise State University

In order to enable further advances in microelectronics, new processes capable of precisely depositing films are required. This is especially true of processes meant for depositing transition metal dichalcogenides such as MoS_2, a material of particular interest due to its high potential mobility even at a thickness of a few atoms. Molybdenum oxide (MoO_x) is a wide bandgap transition metal oxide that has been of growing interest for several different applications in the semiconductor community, including for use as gate dielectrics in ultra-thin transistors, carrier-selective contacts in solar cells, and chemical selective materials in gas detection sensors. In this work, we report on an industry-compatible processes for depositing MoO_x and MoS_x thin films at 200 °C using bis(tert-butylamino)bis(dimethylamino)Mo (BTBDM) with H_2O or H_2S, respectively. Post deposition annealing in oxygen formed MoO3 from MoO_x, while annealing either MoO_x or MoS_x in H_2S formed crystalline MoS_2. ALD processes were characterized using in situ quartz microbalance measurements, while the resulting films were characterized using X-ray photoelectron spectroscopy, atomic force microscopy, optical absorption, Raman spectroscopy, and photoluminescence measurements. These results provide insight into methodologies for both precisely depositing crystalline MoS_2 and its oxide to accelerate the integration of 2D materials into leading edge microelectronics.

EM-MoP-13 Phase Complexity in Two-Dimensional Iron Sulfide on Au(111)*, **Alessandro Baraldi**,* University of Trieste, Italy

Despite extensive research on two-dimensional (2D) materials, almost all experimentally synthesized 2D systems derive from van der Waals crystals. Beyond this class, only a limited number of compounds have so far been theoretically predicted to be stable in the 2D limit [1]. In this context, iron–sulfur compounds have recently emerged as promising candidates. Density functional theory predicts that both hexagonal FeS_2 and tetragonal FeS phases can exist as stable monolayers, exhibiting strain-tunable magnetic properties [2-4]. Although the Mermin-Wagner theorem precludes long-range magnetic order in ideal 2D isotropic systems, magnetic anisotropy can lift this constraint and allow stable ordering, enabling tunable magnetism at the atomic scale [5], which is essential for spintronics [2-4], as well as other emerging phenomena such as topological effects [6], multiferroicity [7], and proximity effects in heterostructures [8]. However, compared to their bulk counterparts, Fe–S systems generally display a rich phase diagram, characterized by multiple stoichiometries and atomic arrangements [9]. A similar complexity may also persist in the 2D limit, highlighting the need for a systematic experimental investigation into which 2D FeS_x phases can actually form. For this purpose, we systematically grow and characterize iron sulfide monolayers on Au(111) via in-situ co-deposition of Fe and S. Low-energy electron diffraction (LEED), scanning tunneling microscopy (STM), and X-ray photoelectron spectroscopy (XPS) reveal two primary phases: one with a hexagonal atomic arrangement consistent with FeS_2, forming a moiré superstructure, and one with a square arrangement. By tuning sulfur exposure, we observe additional phases with varying stoichiometry and atomic arrangement, all belonging to the same 5×5 superstructure family. These results confirm the existence of a complex 2D phase diagram for FeS_x monolayers, establishing them as a versatile and tunable platform for exploring 2D magnetism in non-van der Waals systems.

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EM-MoP-14 Research on New-material Screening Methods toward the Development of Chemical-reaction-based Surface-roughness Reduction Processes, ***Taiki Kato***, *Hirokazu Ueda, Mitsuhiro Tachibana,* Tokyo Electron Ltd., Japan*; Peter Ventzek,* Tokyo Electron Ltd.

In semiconductor device manufacturing processes, substrate surface roughness should be minimized because it leads to increased electrical resistance and added parasitic capacitance. Critical for device scaling, this is even more so when considering two-dimensional materials. Conventional methods for reducing substrate roughness include atomic layer deposition (ALD) and atomic layer etching (ALE), but a method that could reduce only the substrate roughness via surface chemical reactions without changing film thickness would represent a major breakthrough. We developed a numerical analysis method to evaluate the roughness-reduction effects of novel materials. The planarization capability of new precursors on various substrate materials was ranked for different topographic structures. The goal of the study at this stage is to prove the feasibility of chemical planarization of common interconnect metals.

Numerical evaluation of roughness-reduction effects followed two approaches: molecular dynamics (MD) and direct evaluation of the reaction-pathway thermodynamics. First, machine-learned potentials (MLP) based MD simulations described how novel precursor molecules interact on various metal surfaces with different roughness features. The analysis produced a picture in which certain reactive precursors, upon impinging on rough metal substrates, bond with surface metal atoms promoting their mobility, diffusion and surface flattening. By comparing the MD simulation temperature conditions at which metal surfaces become flattenable, we can rank the relative ease of planarization among different metals including ruthenium, cobalt and gold. Our second approach employed reaction-pathway (thermodynamics) to evaluate the activation energy for step-edge collapse for various metal surfaces. Smaller activation energies imply an easier to planarize surface. The same three metals in the MD study were evaluated and found to scale consistently. We also found that adsorption of the novel precursors reduces the activation energy for step-edge collapse, clarifying a mechanism in which precursor adsorption promotes diffusion of surface metal atoms and thereby enables surface planarization.

The presentation summarizes scaling trends we see from simulation-based studies of substrate-roughness adsorbate mediated planarization for various materials. Specifically, we show improvements in device characteristics resulting from reduced substrate surface roughness, experimental evaluations of roughness reduction versus film-thickness change, and potential process applications. We finish with an outlook for future development.

EM-MoP-15 Molecular Layer Deposition of Metalcones Using Salicylaldehyde as an Organic Precursor, ***Henry Yu-Jun Tang***, *Hao-Wei Chan, Bo-Yuan Gu, Zhen-Rou Chang, Fang-Yu Lin, Yi-Jung Liao, Feng-Yu Tsai,* National Taiwan University, Taiwan

This study demonstrates molecular layer deposition (MLD) of alucone and hafnicone thin films using a previously unexplored organic precursor, salicylaldehyde, paired with trimethylaluminum (TMA) and tetrakis(dimethylamido)hafnium(IV) (TDMAHf), respectively. MLD of alucone and hafnicone at deposition temperatures between 120 and 190°C was confirmed with in-situ quartz crystal microbalance (QCM) and chemical analyses. The alucone chemistry was observed to be prone to self-termination, which could be mitigated with two methods: using an exposure process, and using H_2O as a coreactant. Conversely, the hafnicone chemistry showed strong resistance to self-termination owing to the high functionality and large ligand-to-ligand steric hindrance of TDMAHf. The potential of the alucone and hafnicone films as low dielectric constant (k) materials was evaluated, with the alucone and hafnicone films exhibiting k value of 4.2 and 4.7, respectively. The alucone and hafnicone films showed good thermal stability, with ~25% and 20% reduction in thickness upon baking in vacuum at 500°C for 15 min, respectively.

EM-MoP-16 The Effect of Remote Ar Plasmas on the Crystalline Structure of VO_2, *Peter Litwin,* U.S. Naval Research Laboratory*; Neeraj Nepal,* US Naval Research Laboratory*; Andrew Lang,* U.S. Naval Research Laboratory*; David Boris,* US Naval Research Laboratory*; Michael Johnson,* Naval Research Laboratory, USA*; Scott Walton,* US Naval Research Laboratory*;* ***Virginia Wheeler****,* U.S. Naval Research Laboratory

The effect of chemically inert plasmas on the surface of thin film materials is of interest because it allows for an additional means to deliver energy to a material beyond increasing the material's temperature. This could be of use in cases where energy needs to be delivered to specific layers or interfaces in a heterostructure without subjecting the entire material stack to higher temperatures or to overcome energetic barriers, such as those associated with material crystallization (or amorphization) or the formation of metastable phases. However, plasmas make for a complex environment due to the various energy contributions from ions, electrons, excited species, and photons. Despite this complexity, an increased understanding of energy transfer at the plasmas-surface interface opens additional avenues in material engineering. This may be particularly true for plasma enhanced atomic layer deposition (PEALD) processes where deposited thin films are cyclically exposed to plasmas and thus could benefit from an increased understanding of the interaction between plasmas and material surfaces.

In this work we look at the impact of chemically inert remote Ar plasmas on crystalline VO_2 (c-VO_2) thin films deposited by ALD. Thermal ALD of VO_2 was carried out at 150 °C using TEMAV and O_3 and subsequently crystallized in a dedicated thermal annealing vacuum system using our typical process[1]. We demonstrate that under certain plasma conditions we can remove the Raman signature of the c-VO_2 films without any change to the surface morphology of the material, and this capability was greater when operating at lower pressures during the plasma exposure. Additionally, by changing the Ar plasma conditions used, we are also capable of recovering the crystalline nature of the previously damaged films; this was accomplished by treating the sample to subsequent plasma exposures of descending power. This presentation will discuss the details of these experiments and, with the aid of in situ plasma diagnostics, attempt to elucidate the mechanisms responsible for the behavior observed.

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EM-MoP-17 Vapor Phase Infiltration of Metal Oxides into Polymeric Water Treatment Membranes, *Jiaman Wang, Daewon Kim, Soobin Cho,* ***Bezawit Getachew****,* Rice University

Vapor phase infiltration of metal oxides into polymeric membranes may offer a novel way to combine the benefits of polymeric and ceramic membranes and enable improved capabilities in water treatment membranes. In this paper, we investigate the infiltration of alumina into four different types of polymeric membranes used in water treatment, namely, polyamide reverse osmosis membranes, commercial cation and anion exchange membranes, and polyethersulfone ultrafiltration membranes. The infiltration is characterized by using X-ray photoelectron spectroscopy (XPS) to confirm the presence of metal oxide, quantify the amount of incorporation at the surface and as a function of depth, and probe the type of bonding taking place. Complementary SEM-EDX (Scanning Electron Microscopy with Energy Dispersive X-ray Spectroscopy) experiments show the distribution of the inorganic phase within the membranes. We find that bulk infiltration is possible on all types of membranes, with commercial anion exchange membranes and polyethersulfone membranes showing the greatest uptake, while polyamide RO and cation exchange membranes result in greater surface deposition. Preliminary results show that in the case of anion exchange membranes, transport properties are not altered due to infiltration while the stability of the membranes in high pH and hypochlorite environments is greatly improved.

EM-MoP-18 Tunable Phase Change Behavior of VO_2 Thin Films Grown by Atomic Layer Deposition, ***Jeremy Bairan Espano***, *Joe Klesko,* Sandia National Laboratories

Vanadium Dioxide (VO_2) is an emerging phase change material with numerous applications including sensors, transistors, and photonics. Presently however, VO_2 thin films possess synthetic challenges. While established methods of synthesizing VO_2 (e.g. sputter deposition, physical vapor deposition, chemical vapor deposition, and hydrothermal synthesis) have been successful at growing this material phase-pure, these approaches do not support conformal deposition on 3D or high-aspect ratio surfaces. Additionally, tuning the phase change temperature has proven to be costly and not well controlled, with many methods using expensive doping processes (e.g. Ta, Mo, Fe, N) to modulate the transition temperature. In this study, we leverage atomic layer deposition (ALD) to synthesize VO_2, due to its unique ability to grow conformal films with angstrom-level thickness control. By optimizing the post-ALD annealing parameters (e.g. O_2 flow rate/partial pressure, temperature, ramp rate, etc.), we can tune the phase-transition transition temperature and width of the hysteresis. Herein, our exploration of annealing environments, coupled with microscopic and spectroscopic thin film measurements supports precise tunability of thin film VO_2 for next-generation technologies.

EM-MoP-19 Scalable and Controllable Deposition of Extrinsically Doped P-Type MoS_2 via Thermal Atomic Layer Deposition, ***Sungjoon Kim***, *Jeffrey Elam,* Argonne National Laboratory

Computational energy consumption is increasing exponentially, making energy-efficient microelectronics and computing an urgent need. Three-dimensional integrated circuits (3D ICs) and neuromorphic computing promise to revolutionize information technology by drastically reducing the energy consumption of computers, and two-dimensional (2D) semiconductors like molybdenum disulfide (MoS_2) can enable such technologies. However, the development of complementary p-type MoS_2 is needed to fully leverage the benefits of 2D semiconductors. Moreover, thermal processes for thin film deposition are preferred over plasma-based techniques in high aspect ratio applications such as vertical gate-all-around transistors and 3D NAND. Here, we demonstrate the uniform and controlled deposition of extrinsically doped p-type MoS_2 using thermal atomic layer deposition (ALD). By varying the dopant cycle ratio, the final MoS_2's resistivity and charge carrier concentration can be precisely tuned. The resulting p-type MoS_2 was characterized using techniques including Raman spectroscopy, X-ray photoelectron spectroscopy, and Hall measurements, and was used to fabricate and test memtransistors. This work offers a pathway to deposit p-type 2D materials with tailored material properties.

EM-MoP-20 Mechanistic Transformation Pathway to Continuous and Impurity-Free Tellurium Films, ***Seung Ho Ryu***, *Seungsu Kim, Jihoon Jeon, Gwang Min Park, Seong Keun Kim,* Korea University, Republic of Korea

As Si-based devices approach their physical scaling limits, monolithic three-dimensional (M3D) integration has emerged as a promising strategy for continued performance enhancement. In this architecture, transistors are vertically stacked within the back-end-of-line (BEOL) layers, imposing a strict process temperature limit below 400 °C to prevent degradation of front-end CMOS circuits. This restriction necessitates new channel materials that can be processed at low temperatures while maintaining high performance. Although substantial advances have been achieved in n-type oxides such as In_2O_3 and IGZO, the development of BEOL-compatible p-type channels remains limited.

Tellurium (Te) has attracted attention as a promising p-type semiconductor owing to its intrinsically high hole mobility and low melting point. However, direct ALD growth typically yields discontinuous, island-like films due to poor wettability and weak interchain van der Waals bonding. Previous approaches, such as increasing precursor pressure or introducing TeO_2 adhesion layers, have shown limited success because of poor conformality and interfacial oxygen residues. Here, we present a transformation-based strategy in which ALD-deposited TeO_2 is subsequently reduced to elemental Te. This method enables the formation of ultrathin, continuous, and oxygen-free Te layers with excellent conformality. Comprehensive structural and electrical analyses confirm complete phase conversion, smooth morphology, and stable p-type conduction, demonstrating a viable route for BEOL-compatible p-type channel integration in next-generation M3D electronics.

ALD Applications

Room Ybor Salons I-IV - Session AA1-TuM

ALD Interconnect Applications

Moderators: Scott Clendenning, Intel Corporation, **Jin-Seong Park**, Hanyang University

8:00am **AA1-TuM-1 Molybdenum Deposition Chemistry for Advanced Interconnects***, Kyle Blakeney,* Lam Research Corporation **INVITED**

Molybdenum (Mo) stands out among advanced interconnect materials due to its intrinsically low resistivity, strong adhesion, and ability to be integrated without liners or diffusion barriers—features that maximize conductive cross–section as device dimensions continue to shrink. In contrast to tungsten, Mo offers superior resistivity scaling, improved adhesion behavior, and broad compatibility with advanced device architectures. Despite this promise, there are few published Mo ALD reports as most research laboratories cannot readily handle the unique process chemistry and reactor conditions.

The ALD/CVD Metals Product Group at Lam Research has developed Mo deposition technologies targeting interconnect scaling across NAND Flash, DRAM, and logic applications. This presentation will first outline the research strategies that enabled these advances, from modular coupon reactors for rapid pathfinding, to decades of leadership in tungsten ALD.

The second part of the talk will examine Mo precursor surface chemistry, comparing halide–based and metalorganic (MO) approaches. Although metalorganic precursors are commonly used for depositing non–conductor films—including SiO_2, SiN, TiN, and Al_2O_3—they have not matched the performance of chloride–based precursors for depositing high–purity metallic Mo. But the low vapor pressure solid Mo chloride precursors place demands on hardware design to exploit the complex surface chemistry for both conformal and selective deposition, creating new opportunities for barrier–less and bottom–up Mo integration in advanced interconnects.

8:30am **AA1-TuM-3 Thermal Atomic Layer Deposition of Transition Metal Phosphide Thin Films for Interconnects***, John D. Hues,* ***Nolan Olaso****, Wesley Jen,* Micron School of Materials Science and Engineering, Boise State University*; Mehedi Hasan Prince, Sadiq Shahriyar Nishat,* Department of Materials Science and Engineering, Rensselaer Polytechnic Institute*; Steven M. Hues,* Micron School of Materials Science and Engineering, Boise State University, Boise*; Daniel Gall,* Department of Materials Science and Engineering, Rensselaer Polytechnic Institute*; Elton Graugnard,* Micron School of Materials Science and Engineering, Boise State University, Boise

The aggressive scaling of semiconductor technology nodes has pushed copper interconnects to their limit, as the technology approaches its minimum viable dimensions. Further scaling results in unacceptable levels of interconnect resistance due to interface and grain boundary scattering, which degrades device performance and power consumption metrics. The proliferation of generative artificial intelligence and cloud computing threatens to strain this relationship further as demand for high-performance logic and memory devices rises sharply. To better meet this demand, alternative interconnect materials must be investigated. One family of materials being explored is topological metals, which are predicted to have favorable resistivity scaling largely due to their topologically protected surface states, which suppress electron scattering in nanoscale films. We report on novel thermal atomic layer deposition (ALD) chemistries for various phosphide-based topological metals, specifically molybdenum phosphide (MoP) and niobium phosphide (NbP) using molybdenum(V) chloride (MoCl5), niobium(V) chloride (NbCl5) and tris(dimethylamino)phosphine (TDMAP) between at 325 to 400 °C. The resulting films were characterized using ex-situ X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), scanning electron microscopy (SEM), and four-point probe measurements. Film composition was confirmed through XPS chemical state analysis to be near-stoichiometric (1:1). Four-point probe measurements of the as-deposited films indicated non-ideal electrical performance, which was subsequently improved through post-deposition annealing. While additional work is required to further improve the electrical performance of these materials, these new ALD chemistries may provide a scalable, BEOL-compatible method for the deposition of next-generation interconnect materials.

8:45am **AA1-TuM-4 Low Resistivity Metallic Films by Thermal Atomic Layer Deposition Enabling Next Generation Interconnects***, Sara Harris,* Forge Nano*; Thomas P. Moffat,* NIST*; Matthew S. Weimer, Dane Lindblad,* Forge Nano*; Daniel Josell,* NIST*; Arreliane Dameron,* Forge Nano

Device miniaturization continues to push technological boundaries, requiring constant evolution in transistor material systems, architecture, and manufacturing processes. To fully actualize bleeding edge (two to three nanometer) transistor capabilities, integrated circuit (IC) manufacturing must keep pace. Back end of line (BOEL) fabrication poses several challenges to chip scaling: most notoriously the copper bottleneck in which thick barrier layers and resistance capacitance (RC) delays limit functional interconnect pitch to 21 nanometers [1]. To overcome this critical barrier, low resistivity, conformal metal films have been studied for hybrid metallization; decreasing interconnect resistance and reducing barrier layer thicknesses. As interconnect pitch decreases traditional PVD copper barrier/seed layers are limited by line of sight and experience pinch off and void formation [2]. Expanding on the ruthenium (Ru) ALD copper seed layers presented last year, this work explores the use of low resistivity thermal ALD iridium (Ir) to enable next generation interconnects. Thermal ALD Ir and Ru deposited at 250 °C both demonstrate conformal deposition on 10:1 aspect ratio through glass vias (TGVs) and show void free copper fill using a cyclic pulsed electrochemical deposition (ECD) process. As expected, the primary difference between the Ir and Ru is electrical resistivity. Seed film resistivity as deposited on TGVs was measured using four-point probe; 10 nm of Ru measured 41 μΩ·cm and 10 nm of Ir measured 16 μΩ·cm. Successful copper ECD was demonstrated with 10 nm of Ir (resistivity 16 μΩ·cm) and 20 nm of Ru (resistivity 22 μΩ·cm). The full layer stack for these films and conformal TGV Cu fill is shown in *Figure 1*. Reduction in required layer thickness combined with improved electrical properties and demonstrated conformality could serve as crucial steps forward for advanced interconnects and BEOL architecture. Additionally, this work compares Ir film quality as deposited at 250 °C and 300 °C. Ir deposited at 300 °C exhibits improved environmental stability when compared to 250 °C Ir as measured with 4-point probe after aging in atmosphere over several months. 300 °C Ir also shows a shortened nucleation delay, and optical constants (n and k) more closely aligned to bulk Ir values, as measured with spectroscopic ellipsometry. Ir film characterization for both temperatures including XPS, XRR, XRD and AFM is ongoing, and will be presented.

9:00am **AA1-TuM-5 Investigating TaN-Doped Ru Film Using ALD and Pulsed CVD Process for Enhanced BEOL Interconnects Performance in Logic Device***, Juhyeon Lee, Hyun Cho, Jungmin Lee, Wonhyuk Hong, Hyeonseok Do, Jongkwan Lee, Jihwan Lee, Yoonsuk Kim, Eunji Jung,* Samsung Electronics Co., Republic of Korea

As BEOL interconnect dimensions continue to scale, aggressive reduction of barrier and liner thickness is critical for enabling Cu fill scalability. Conventional TaN-based schemes require an additional liner layer with a minimum thickness to ensure stable Cu reflow, which fundamentally limits total barrier thickness scaling and motivates the development of alternative, highly scalable barrier materials.

In this work, a Ru-rich TaN-doped diffusion barrier was designed and optimized through simulation, with a particular focus on the Ru/Ta composition ratio. Three key parameters were systematically investigated as a function of Ru content: (1) relative energy mapping of Cu diffusion pathways, (2) stability of residual Cu atoms within the barrier structure, and (3) formation-energy differences between crystalline and amorphous phases. Based on these analyses, an optimized Ru/Ta ratio predicted to form an amorphous and continuous TaN-doped Ru barrier film was identified.

To validate these findings, the optimized composition was deposited using a hybrid process combining atomic layer deposition (ALD) and pulsed chemical vapor deposition (CVD). To overcome the nucleation challenges and island growth typically associated with CVD-type Ru precursors, a pulsed injection scheme was employed to promote high-density nucleation and ensure superior film continuity at the ultrathin regime. The film composition and sub-20 Å thickness were confirmed by XPS and XRF, respectively, enabling precise evaluation of composition-dependent properties.

Reliability evaluations demonstrated that the TaN-doped Ru films provide a robust diffusion barrier. The films exhibited significantly enhanced time-dependent dielectric breakdown (TDDB) characteristics and electromigration (EM) lifetimes exceeding 10 years. These results demonstrate that the TaN-doped Ru diffusion barrier deposited by ALD and

pulse CVD provides an effective and scalable solution for ultrathin BEOL interconnects, making it a promising candidate for advanced logic technology nodes.

9:15am **AA1-TuM-6 Low-Resistivity Ruthenium Thin Films with Enhanced Surface Morphology via High-Temperature 6-Step Atomic Layer Deposition for Advanced Interconnect Applications**, ***Dahyeon Park,*** *Jeongha Kim, Soohyun Kim,* Ulsan National Institute of Science and Technology (UNIST), Republic of Korea

As semiconductor devices continue to scale, the increase in interconnect resistance has emerged as a major bottleneck limiting device performance. Ruthenium (Ru) is attracting attention as a promising candidate to replace conventional copper (Cu) and tungsten (W) interconnects due to its low bulk resistivity and superior resistance to electromigration. Meanwhile, the electrical properties of Ru thin films are reported to depend heavily on microstructural factors such as crystallinity and impurity distribution, and relatively high deposition temperatures are known to be advantageous for improving these properties. However, high-temperature atomic layer deposition (ALD) requires both thermal stability of the precursor and precise control of surface reactions, which has acted as a significant technical constraint in conventional Ru ALD processes.

The recently reported Ru precursor, [Ru(trimethylenemethane (TMM))(*p*-cymene)], exhibits excellent thermal stability up to approximately 400 °C, offering the advantage of applicability in high-temperature processes. However, when the process temperature increases beyond a certain level, the resistivity of the thin film actually increases due to enhanced electron scattering caused by increased surface roughness. This suggests the need for a process design capable of effectively controlling surface morphology while maintaining the benefits of high-temperature processing.

In this study, we propose a high-quality Ru thin film deposition process via a 6-step ALD utilizing a [Ru(TMM))(*p*-cymene)] precursor and a sequential H_2–O_2 injection strategy. The Ru thin films deposited using the optimized 6-step process exhibited a resistivity of 15.5 μΩ·cm at a thickness of approximately 20 nm, a significant improvement compared to the 18.2 μΩ·cm of the conventional 4-step process. This reduction in resistivity is attributed to the mitigation of electron scattering resulting from the improvement in surface roughness.

Furthermore, the optimized process achieved 100% step coverage with uniform thickness distribution even in nanoscale trench patterns. These results demonstrate the potential of the 6-step ALD process to mitigate the limitations posed by next-generation interconnect scaling while maintaining low resistivity characteristics.

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Acknowledgements

This work was supported by the Technology Innovation Program (RS-2023-00236667, K-CHIPS) funded by the Ministry of Trade, Industry & Energy (MOTIE, Korea).

9:30am **AA1-TuM-7 Atomic Layer Modulation for Compositionally Controlled Ruzno Films as Diffusion Barriers for Cu Interconnects**, ***Yeseul Son,*** *Ulsan National Institute of Science and Technology, UNIST, Republic of Korea; Soo-Hyun Kim,* Ulsan National Instititute of Science and Technology, UNIST, Republic of Korea*; Jeongha Kim, Minwoo Kim, Sang Bok Kim,* Ulsan National Institute of Science and Technology, UNIST, Republic of Korea

Atomic layer modulation (ALM) was employed as an ALD-based process strategy to enable compound thin-film formation with precise compositional control. In ALM, multiple metal precursors are sequentially introduced within a single ALD cycle, followed by a common reactant step, allowing atomic-scale mixing of multi-component systems while retaining the precise thickness control, excellent uniformity, and cycle-to-cycle reproducibility characteristic of ALD processes. Based on this capability, RuZnO thin films were synthesized and investigated as diffusion barrier layers for Cu interconnects. RuZnO was selected to combine the favorable properties of Ru, such as thermal stability and a short electron mean free path, with the ability of ZnO to enhance adhesion at dielectric interfaces through zinc silicate formation, thereby integrating diffusion suppression and interfacial stability within a single layer. RuZnO films were deposited using tricarbonyl(trimethylenemethane)ruthenium [Ru(TMM)$(CO)_3$] and diethylzinc (DEZ) as precursors, and O_2 as a reactant. The Ru–Zn–O composition was systematically varied by controlling the ALM process's various parameters. The structural properties, thickness uniformity, and compositional distribution of the ALM-grown films were analyzed using XRD, XRR, RBS, and TEM. The results confirm the formation of homogeneous RuZnO layers over a range of compositions, indicating effective atomic-scale mixing achieved within the ALM cycle. Based on these results, compositionally controlled RuZnO films grown by ALM are discussed as diffusion barrier layers for Cu interconnects, and the detailed results will be presented at the conference.

9:45am **AA1-TuM-8 A 2-step Platinum Atomic Layer Deposition Process for Suppressing Interfacial Oxidation in Advanced Interconnect Applications**, ***Jeongha Kim,*** *Yeseul Son, Soo-Hyun Kim,* Ulsan National Institute of Science and Technology, Republic of Korea

The continuous scaling of copper (Cu) interconnects has resulted in a sharp increase in resistivity due to enhanced surface and grainboundary scattering, highlighting the need for alternative metals for next-generation interconnects [1]. According to the Fuchs–Sondheimer (FS) and Mayadas–Shatzkes (MS) model, larger grain sizes reduce grainboundary scattering, thereby enabling lower resistivity [2]. Among various candidate metals, platinum (Pt)offers an advantage over othernoble metals such as ruthenium (Ru) in that its lower melting temperature allows the formation of larger grains at the same atomic layer deposition (ALD) process temperature [3]. However, while O_2-based metal ALD processes can achieve low resistivity films, they can induce interfacial oxidation of the underlying layers. In contrast, H_2-based metal ALD effectively suppresses interfacial oxidation but typically results in relatively high resistivity [4].

To overcome this trade-off, we propose a 2-step Pt ALD process consisting of an H_2-based nucleation step followed by an O_2-based Pt deposition step. Experimental results show that the H_2 process effectively suppresses interfacial oxidation while maintaining the quality of Pt films. Although the as-deposition films exhibit relatively high resistivity, post-deposition annealing reduces the resistivity by approximately 52%. The proposed 2-step Pt ALD process enables the formation of low-resistivity Pt films while minimizing interfacial oxidation and is experimentally demonstrated to be effective in mitigating scaling effects. Compared to the process using only an O_2 reactant, the proposed approach achieves lower resistivity in thinner Pt films, highlighting its potential as a promising process for next-generation interconnect technology.

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Acknowledgements

This work was supported by the Technology Innovation Program (Public-private joint investment semiconductor R&D program, K-CHIPS) to foster high-quality human resources, funded by the Ministry of Trade, Industry & Energy (MOTIE, Korea) (Grant No. RS-2023-00236667, High-performance Ru-TiN interconnects via high-temperature atomic layer deposition (ALD) and development of new ALD-based interconnect materials; and Grant No. RS-2025-02311098, Area-selective deposition of novel metals with 100% selectivity for Si interconnect technology).

ALD Applications
Room Ybor Salons I-IV - Session AA2-TuM

ALD Dielectric Applications

Moderators: Olasehinde Owoseni, Intel, **Seung-Yeul Yang**, Samsung

10:45am **AA2-TuM-12 Sub-5 nm Indium Oxynitride Channel in Top-gated FETs Fabricated by PEALD for High-Performance 3D Transistor**, ***Doo San Kim***, *Minjong Lee, Soham Shirodkar,* The University of Texas at Dallas*; Min Gyeong Jo,* Hanyang University, Republic of Korea*; Thi Thu Huong Chu, Dushyant Narayan, Dan Le,* The University of Texas at Dallas*; Youngbae Ahn, Ja-Yong Kim, Seung Wook Ryu,* SK hynix, Republic of Korea*; Jiyoung Kim,* The University of Texas at Dallas

As silicon scaling approaches its physical limits, indium-based oxide semiconductors have emerged as promising channel materials because they maintain high carrier mobility and drive current even at channel thickness below 5 nm, enabling superior scalability. Among them, In_2O_3 exhibits excellent drive current; however, hydrogen incorporation leads to hydroxyl (OH) formation, resulting in device instability and threshold voltage shifts. Incorporating nitrogen to form indium oxynitride (InON) is expected to enhance mobility while effectively suppressing the formation of hydrogen induced OH bonds, thereby improving device stability.

Despite these advantages, direct deposition of InON via atomic layer deposition (ALD) is challenging because the bonding dissociation energy of In-O (~346 kJ/mol) is significantly stronger than that of In-N (~186 kJ/mol), making it difficult to incorporate sufficient nitrogen during the simultaneous supply of oxygen and nitrogen reactants.[1,2] In this work, we propose a two-step channel formation strategy: the initial deposition of an indium nitride (InN) thin film followed by an oxidation process to convert it into an InON channel layer.

In this presentation, we report the deposition of sub-5 nm conformal InN films via Hollow-Cathode Plasma (HCP)-enhanced ALD at 240 °C. To improve the structural and electrical stability of the channel, an annealing-based oxidation process was applied, converting InN into the more robust InON and evaluating their integration into top-gated (TG) thin-film transistor (TFT) devices. We investigated the influence of process parameters such as plasma power, process pressure, and deposition temperature for the film characteristics. The 5 nm InON layer was deposited at 240 °C, followed by the deposition of a 5 nm hafnium zirconium oxide (HZO) dielectric layer, and finally a TG-FET was demonstrated using Ni metal contacts. We presented InON TG-FET results, including transfer and output characteristics, temperature dependence, and channel length scaling. Our findings demonstrate that InON-based TFTs with a 100nm channel length achieve an on-current of ~1.2mA/μm at V_D = 1 V, an I_{on}/I_{off} ratio exceeding 10^9, and a contact resistivitywith Ni of 4 x $10^{-8}\Omega\cdot cm^2$. In addition, the $\triangle V_{th}$ under positive and negative bias stress is 90 and 15 mV, at V_{ov} = ±1 V.

This work was supported by SK hynix Inc.

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11:00am **AA2-TuM-13 V_{Fb} Control Technique of SiO_2/Dipole/$HfZrO_2$ Stack Structure Using New LaTiO and AlTiO Dipoles**, ***Tomomi Sawada***, *Toshihide Nabatame, Hiromi Miura, Manami Miyamoto, Takashi Onaya, Kazuhito Tsukagoshi, Naoki Fukata, Wipakorn Jevasuwan,* National Institute for Materials Science (NIMS), Japan*; Shinji Migita,* National Institute of Advanced Industrial Science and Technology (AIST), Japan

Dipole technique has been widely investigated to control the threshold voltage (V_{th}) of metal/High-k CMOS with GAA gate stack in 50 mV increments. La_2O_3 and Al_2O_3 are generally employed as n- and p-type dipoles. However, it remains a big issue of a large V_{th} shift in the sub-nm region of the dipole layer. In this paper, we investigated flatband voltage (V_{fb}) shift for SiO_2/dipole/$HfZrO_2$ stack structure using new LaTiO and AlTiO as n- and p-type dipoles.

p-Si/SiO_2/dipole/$HfZrO_2$/Au capacitor was fabricated at a maximum process temperature of 400 °C as follows: La_2O_3, TiO_2 and Al_2O_3 dipole layers were deposited on p-Si/SiO_2 (3.6 nm) by ALD at 250 °C with H_2O and La(iPrCp)$_3$, TDMAT, and TMA, respectively. LaTiO and AlTiO dipoles were also prepared by changing each ALD cycle of La_2O_3 and TiO_2, and Al_2O_3 and TiO_2 by ALD at 250 °C with H_2O, respectively. Next, an $HfZrO_2$ (2 nm) film was deposited on dipole layer by ALD at 250 °C using TEMA(Hf/Zr)(Hf/Zr = 1/1) cocktail and H_2O. Au gate electrode was deposited on $HfZrO_2$ film to form capacitor. Finally, forming gas annealing was carried out at 400 °C in 3%H_2.

The La_2O_3 and Al_2O_3 dipole capacitors exhibited negative and positive V_{fb} shifts as the La_2O_3 and Al_2O_3 dipole thickness increased, respectively. The V_{fb} shifts for the La_2O_3 and Al_2O_3 dipole capacitors were almost saturated, showing -0.35 and +0.32 V, respectively, when the dipole thickness was 0.8 nm. On the other hand, the TiO_2 dipole capacitor exhibited a V_{fb} shift of nearly 0 V regardless of the dipole thickness. This is due to differences in the strength and direction of the dipoles of La_2O_3, Al_2O_3 and TiO_2 at the SiO_2/dipole interface. The LaTiO (La = 0.46) dipole capacitors reduced the negative V_{fb} shift from -0.29 to -0.11 V compared to the La_2O_3 dipole capacitors when the dipole thickness was 0.2 nm. With a 0.2 nm thick dipole, the AlTiO (Al = 0.62) dipole capacitors also reduced the positive V_{fb} shift by approximately 25% compared to the Al_2O_3 dipole capacitors. This indicates that the dipole strength of La_2O_3 and Al_2O_3 can be effectively reduced by adding TiO_2 without dipole effect. In the LaTiO and AlTiO dipole capacitors, La and Ti atoms, and Al and Ti atoms, respectively, were piled up at the SiO_2/$HfZrO_2$ interface using STEM and EDS analysis. By employing new LaTiO and AlTiO dipoles in addition to La_2O_3 and Al_2O_3, V_{fb} controllability could be enhanced in the sub-nm region of the dipole layer. This is because TiO_2 without the dipole effect was added. This presentation is partially based on the results of the post-5G project (JPNP20017), entrusted to LSTC, commissioned by NEDO.

11:15am **AA2-TuM-14 Low-Temperature High-Pressure Deuterium Annealing for Defect Passivation in ALD-Deposited HfO_2 High-k Film**, ***Ji-Yeon Park***, *Seok-Won Lim, Gi-Beom Park, Chang-Kyun Park, Jin-Seong Park,* Hanyang University, Korea

Atomic layer deposition (ALD) is a key process technology for integrating high-k gate dielectrics into advanced semiconductor devices, providing excellent thickness control, compositional uniformity, and conformality. As conventional SiO_2 gate dielectrics reach their physical scaling limits due to increased direct tunneling leakage, high-k materials such as HfO_2 have been widely adopted [1]. Although ALD enables the formation of high-quality HfO_2 thin films, device performance is strongly influenced by defect states formed at the HfO_2/Si interface [2].In this study, ALD-deposited HfO_2 thin films grown using a Cp-Hf/O_3 process were investigated with a focus on the correlation between HfO_2/Si interfacial defect and electrical characteristics. Post-deposition deuterium treatment was employed not to modify the intrinsic quality of the ALD film, but as a post-ALD interface engineering and analytical tool to evaluate and improve defect states located at or near the interface. Electrical characterization using C–V and J–E measurements showed reductions in interface trap density, improved flat-band voltage stability, decreased leakage current density, and enhanced breakdown field after deuterium treatment, suggesting effective passivation of interface-related defects. Secondary ion mass spectrometry (SIMS) and X-ray photoelectron spectroscopy (XPS) analyses were conducted to examine deuterium incorporation behavior and changes in chemical bonding states, and their relationship to the observed electrical improvements was analyzed. These results indicate that the electrical performance of ALD-grown HfO_2 high-k dielectrics is governed primarily by interface quality rather than bulk film limitations. This work highlights the importance of post-ALD interface engineering and provides insight into ALD-compatible strategies for achieving reliable high-k/Si interfaces in next-generation semiconductor devices.Reference1) Wilk, Glen D., Robert M. Wallace, and JáM Anthony. "High-κ gate dielectrics: Current status and materials properties considerations." Journal of applied physics 89.10 (2001): 5243-5275. 2) E. P. Gusev,et al " Ultrathin high-k gate stacks for advanced CMOS devices," Microelectronic Engineering 69 (2003): 145-151.

11:30am **AA2-TuM-15 Infiltration of Porous SiOCH Thin Films by High-k Materials: Toward Nanocomposites with Enhanced Dielectric Properties**, ***Julie Chaussard***, *Stéphane Cadot, Marc Veillerot, Hélène Coudert-Alteirac, Nicolas Gauthier, Nicolas Bernier, Chloé Guérin, Aude Lefèvre,* CEA/LETI-University Grenoble Alpes, France*; Patrice Gonon,* Université Grenoble Alpes, CNRS, France*; Vincent Jousseaume,* CEA/LETI-University Grenoble Alpes, France

Dielectric materials, especially insulating polymers, are crucial for various technological applications due to their high breakdown voltage and low cost [1]. However, they generally exhibit low dielectric constant and thermal stability, limiting their use in field as power electronics.

To enhance their dielectric constant, recent studies have explored the elaboration of nanocomposites by adding alumina nanoparticles into a polymer matrix, resulting in significant improvements in dielectric constant and breakdown voltage even at low concentrations [2]. Despite these promising results, the elaboration methods used were incompatible with standard microelectronic processes.

This work studies the elaboration of nanocomposite thin films using microelectronic materials stable up to 400°C, deposited by vacuum deposition techniques. To this end, 100 nm porous SiOCH were deposited by PE-CVD on Si wafers using a porogen approach [3]. Then high-k material was infiltrated into this porous thin film using ALD. The filling process for different materials and precursors was characterized using physicochemical methods (XRF, ellipsometry, XRR, ToF-SIMS, FTIR, TEM). Then, the electrical properties were studied (dielectric constant, dielectric losses, breakdown voltage). In the case of trimethylaluminum/O_3, the results highlight that the filling of the nanometric pores of the porous SiOCH occurs in the first ALD cycles (<5). Using an optimized recipe, a maximum filling of ≈50% of the porosity was obtained. As the number of cycles increases, high-k growth continues on the surface at a rate similar to that observed on Si. FTIR analysis reveals the formation of -OH groups in the first cycles, which increases dielectric constant and dielectric losses. A similar behavior is observed when using H_2O as oxidant. However, after 25 ALD cycles, the disappearance of -OH groups is observed for the TMA/O_3 process. One hypothesis is that the alumina layer formed on top of the porous structure becomes thick enough to limit H_2O adsorption into the matrix. This leads to the elaboration of composites with a dielectric constant 42% higher than that of the porous matrix while maintaining low dielectric losses. Finally, infiltration of porous SiOCH with HfO_2 and $HfZrO_2$ (from chlorinated precursors and water), which have higher dielectric constant than Al_2O_3, also enables enhanced dielectric properties without the presence of -OH groups. But in this case the filling rate is slightly lower than that observed with alumina.

In conclusion, this work demonstrates an easy approach for the elaboration of nanocomposites using standard microelectronic materials to achieve a broader range of electrical properties.

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11:45am **AA2-TuM-16 Electrical Characterization of High-k ALD TiO_2 on AlGaN/GaN HEMT Structures**, ***Neeraj Nepal**, James G. Champlain, Vikrant J. Gokhale, Peter M Litwin, Brian P Downey, Virginia D Wheeler,* U.S. Naval Research Laboratory

Transport and breakdown field characteristics of GaN-based HEMT technologies are limited by high and non-uniform peak electric fields at the drain-edge of the gate. The non-uniform peak field causes premature electric field induced breakdown limiting the device performance [1]. These deleterious effects can be mitigated by integrating films with high dielectric constants (high-k, >20), such as TiO_2 [2-4]. For HEMTs, increased k leads to increased power handling capability without significant reduction in operation frequency. Thus, the goal is to integrate the highest k material possible. ALD provides flexibility in device design, integration and back-end-of line compatibility, making it a promising route for these high-k films. However, ALD high-k dielectrics with ideal interfaces and reduced trapping on AlGaN/GaN HEMTs have not been reported. In this talk, we report on the optimization and electrical characterization of the ALD TiO_2 interface with AlGaN-barrier HEMT structures.

Previously optimized deposition parameters [3] served as the baseline to further optimize electrical performance by pretreating the dielectric-barrier interface of $Al_{0.25}Ga_{0.75}N$/GaN HEMT structures. *Ex-situ* pretreatments including NH_4OH, UV O_3+BOE, piranha and O_2 plasma descum were studied. Similarly, *in-situ* UHV annealing, plasma treatments and their combinations were also studied. The optimum interface was found to be a combination of *ex-situ* O_2-plasma descum and *in-situ* H_2 and N_2 plasma treatments. Initial results using this preparation, a 20nm TiO_2 film demonstrated a reduction in gate leakage by 10^5 compared to a Schottky gate,zero CV hysteresis, a dielectric constant ≥ 50, and no significant change in 2DEG density. Even though the ALD TiO_2 has a narrower bandgap than AlGaN-barrier material, its large dielectric constant provides a pathway forward for dielectric permittivity engineering within the device structure. This engineering approach can improve breakdown voltage, lowers gate leakage and minimizes non-ideality over the state-of-the-art.

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ALD Fundamentals: Growth and Characterization
Room HB Plant Ballroom - Session AF1-TuM

ALD Precursor Design II

Moderators: Seán Barry, Carleton University, Canada, **Charles H. Winter**, Wayne State University

8:00am **AF1-TuM-1 Development in Thermal ALD Chemistry since 2010**, ***Markku Leskelä**,* University of Helsinki, Finland*; Georgi Popov,* ASM Microchemistry Ltd., Finland*; Miika Mattinen, Mikko Ritala,* University of Helsinki, Finland

We recently published a review on the recent trends in thermal ALD chemistry (1). The review highlighted new ALD precursors and process chemistries based on the ALD database found in atomiclimits.com (2) until the end of 2023. The paper compared the processes published before 2010 (769 processes) to those published after 2010 (942 processes). The number of materials deposited by thermal ALD shows steady increase being 227 before 2010 and reaching 539 at the end of 2023. The most popular material group is oxides which are processed both as binary and ternary compounds.

The ALD process development can be divided to two categories: curiosity and application driven research. In the curiosity driven research the aim is to expand the portfolio of ALD processes by adding new elements and materials to the portfolio. From recent literature ALD processes for less common elements Be, Re, Os can be mentioned. However, the development of new ALD processes is clearly more application-driven and motivated by the most important application areas of ALD: microelectronics, energy technology, and catalysis. Need of new materials in these applications is seen in increased intensity of the development of ALD processes for metals, 2D transition metal dichalogenides, and halides

Metal halides, alkoxides, alkyl compounds, β-diketonates, and amides/imides are traditional ALD metal precursors. After 2010, amides/imides have increased their importance in new ALD processes. However, heteroleptic complexes containing two or more above mentioned ligands are the largest precursor type in new processes. Metal processes require the use of reducing agents and therefore research on novel reducing agents is vital.

In the presentation we summarize our most important findings from ALD literature between 2010 and 2023 and highlight the newest results from the last two years. The number of published new processes in 2024-2025 seems to stay at the level of the previous years.

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8:15am **AF1-TuM-2 Designing Stable Organosilane Precursors for High Quality Silicon Oxide**, ***Taylor Hayes**, Anjli Patel, Matthew MacDonald, Manchao Xiao, Haripin Chandra,* EMD Electronics, The Electronics business of Merck KGaA, Darmstadt, Germany

High-quality silicon oxide in a 3D NAND structure is an important material used as an electrical insulator and to form charge trap layers. Additionally, due to the nature of the 3D NAND structure, which achieves an extremely high aspect ratio with several hundred layers, atomic layer deposition (ALD) is critical for obtaining a conformal, high-quality SiO_2 film.

In general, process temperature correlates with film quality; higher process temperatures yield higher quality films. However, in ALD depositions, higher process temperatures necessitate that the organosilane precursor remains stable and self-limiting.

In this paper, we will discuss methods to improve the thermal stability of common organosilane precursors, such as tris(dimethylamino)silane (3DMAS), and evaluate decomposition mechanisms using density functional theory (DFT) modeling.

The Si–H bond in 3DMAS is the weakest link and is prone to thermal decomposition. Replacing the Si–H bond with a Si–CH_3 bond, as seen in tris(dimethylamino)methylsilane (3DMAMS), enhances thermal stability by reducing the energetic feasibility of decomposition pathways. Furthermore, substituting the amino group with a CH_3 group, as in dimethylaminotrimethylsilane (DMATMS), also improves precursor thermal stability.

This paper will explore how higher deposition temperatures and molecular structure significantly influence the experimental film properties achieved using 3DMAS, 3DMAMS, and DMATMS.

8:30am **AF1-TuM-3 Development of Novel Liquid Zr Precursors with Excellent Thermal Stability for High-Temperature ALD Processes in Next-Generation DRAM Capacitors**, ***Taeyoung Lee**, Sunyoung Baik, Sungjun Ji, Shinbeom Kim, Woongjin Choi, Kunhee Kim, Yiun Park, Sangbum Han,* EGTM Co., Ltd. R&D Center, Republic of Korea

With the continuous scaling of DRAM devices, dielectric materials that possess both excellent conformality in high aspect ratio structures and high dielectric constants (high-k) have become increasingly critical. Typically, high-temperature deposition processes are essential for the formation of the tetragonal phase of ZrO_2 thin films, which maximizes the dielectric constant. However, conventional cyclopentadienyl (Cp)-based Zr precursors suffer from limited thermal stability at high temperatures, leading to significant issues such as carbon impurity incorporation and particle generation. To address these challenges, we developed a novel liquid Zr precursor (EGTM Zr) with significantly improved thermal stability compared to conventional precursors. Thermal analysis (TGA and DSC) and visual thermal stability tests confirmed that EGTM Zr exhibited negligible discoloration or decomposition residues even after prolonged exposure to temperatures exceeding 200°C. Furthermore, its thermal decomposition temperature was 312°C, approximately 10°C higher than that of the conventional Cp-Zr precursor. Notably, ALD process evaluations demonstrated that the EGTM Zr precursor has a wider ALD process window of 280–380 °C, which is approximately 80°C wider than that of the reference precursor due to its enhanced thermal stability. This wider window allows for higher process temperatures, which promotes the formation of the high-k tetragonal crystalline phase instead of the lower-k amorphous phase, thereby enhancing device performance. Moreover, thanks to its excellent thermal stability, the EGTM Zr precursor can effectively eliminate issues related to carbon impurity incorporation and particle generation. Additionally, the precursor demonstrated superior step coverage compared to the reference, while the widened process window enables the deposition of high-quality, uniform thin films. Consequently, the EGTM Zr developed in this study is expected to be a promising candidate for next-generation high-performance DRAM capacitor applications.

8:45am **AF1-TuM-4 A New Zinc Amidinate Precursor for Thermal and Plasma-Enhanced ALD of ZnO**, ***Pierre-Alexandre Escarcega**, Jean-Pierre Glauber, Lars Giebeler, Harish Parala, Anjana Devi,* IFW Dresden, Germany

As an n-type semiconductor with remarkable electronic and optical properties, zinc oxide (ZnO) is applicable for various applications. Its wide direct bandgap of 3.3 eV and large exciton binding energy of about 60 meV make it especially promising for use in optoelectronics.[1] Further attributes, including high electron mobility, optical transparency, piezoelectricity, and biocompatibility, render it a versatile material fordiverse technological applications, includingchannel layer in thin-film transistors (TFTs)[2,3] or sensing.[4] However, the integration and efficiency of ZnO in advanced technologies depend on overcoming fabrication challenges to reliably produce high-quality, high-purity thin films and nanostructures. In this regard, atomic layer deposition (ALD) and its variant, plasma-enhanced ALD (PEALD),[5] were shown to enable the deposition of high-quality, stoichiometric, and conformal films, with atomic-level control over film thickness, even at low temperatures. Despite the sophistication of such deposition techniques, developing advanced processes requires new precursors with optimized properties to broaden process windows and enhance film characteristics.

Our group recently reported a versatile Zn precursor, $[Zn(DMP)_2]$,[6] a non-pyrophoric alternative to the widely used DEZ, enabling the growth of high-purity ZnO thin films via ALD and PEALD over a broad temperature range. The ZnO thin films were mainly amorphous or of low crystallinity. In our recent attempts to identify new Zn precursors that can enable crystalline ZnO layers at low temperatures, we were successful in synthesizing bis(N,N'diisopropylacetamidinato)zinc, $[Zn(dpamd)_2]$. The target compound was successfully synthesized by stabilizing the central zinc atom through the delocalized π system of the amidinate ligand backbone.[7]While this ligand enhances the thermal stability, its all-nitrogen coordination guarantees sufficient reactivity.

$[Zn(dpamd)_2]$ is a volatile compound with physico-chemical properties suitable for both thermal and plasma ALD. Additionally, its synthesis can be scaled up, and it is non-pyrophoric, a significant advantage for safety and handling. The thermal properties of $[Zn(dpamd)_2]$ were examined using thermogravimetric analysis (TGA) (Figure 1), which showed promising evaporation behavior. Based on these results, $[Zn(dpamd)_2]$ was used in a thermal ALD process with water as the co-reactant, as well as in a PEALD process with O_2 plasma as the co-reactant. Both methods yielded stoichiometric, high-purity ZnO thin films on Si(100) substrates with self-limiting growth, confirming $[Zn(dpamd)_2]$ as a promising and versatile new ALD precursor.

9:00am **AF1-TuM-5 Amidates and Dimethylaminopropyl Groups as Innovative Ligands: New Opportunities for Ru Precursors**, ***Jorit Obenlüneschloß**,* Leibniz Institute, IFW Dresden, Germany*; Niklas Huster,* Ruhr University Bochum, Germany*; Harish Parala,* Leibniz Institute, IFW Dresden, Germany*; Michael Gock, Michael Unkrig-Bau, Detlef Gaiser,* Heraeus Precious Metals GmbH & Co. KG, Germany*; Anjana Devi,* Leibniz Institute, IFW Dresden, Germany

As the semiconductor industry moves to the 2 nm node and below, Cu as well-established interconnect material in integrated circuits (IC's), is reaching its limits due to diffusion and electromigration. Ru is the most promising replacement candidate in next-generation microchips as the interconnect metal.[1] Its resistivity is less dependent on thickness than that of Cu and Ru can be introduced without liner or diffusion barrier layers.[2] A reduction of up to 60% in resistance is expected when Ru vias are used with Cu wires.[3]

To deposit thin films uniformly on complex-structured substrates, such as those in next-generation gate-all-around field-effect transistors (GAAFETs), atomic layer deposition (ALD) is the preferred method. However, finding suitable Ru precursors that meet ALD requirements, such as high vapor pressure, thermal stability, and high reactivity, is a challenging task for researchers in both academia and industry.

Herein, we showcase and compare two Ru precursors with novel ligand concepts:**[η5-CpRu(CO)$_2$(DMP)]** or dicarbonyl(η5-cyclopentadienyl)(3-dimethylaminopropyl)ruthenium, trade name **HeRu31**,[4]and **[Ru(CO)$_2$(N-*s*BuiPrAD)$_2$]** or dicarbonyl bis(*sec*-butylisopropylamidate)ruthenium, trade name **HeRu43**.[5] The former combines the proven half-sandwich structure dominated by a Cp ring with an aminopropyl ligand, which enhances the compound's stability while maintaining excellent reactivity. The reactive Ru-C bonds of this precursor enable facile deposition of Ru metal. The latter precursor relies on the 1,3-N,O-chelating amidate ligand. Introducing mixed N,O-coordination is a promising approach to prevent carbon contamination in deposited thin films. This coordination should also enable facile deposition via the Ru-N bond.

Employing both concepts, complexes with promising thermal properties for ALD have been obtained, as evidenced by TGA (Fig. 1). Both classes are liquid at room temperature, a highly desirable trait for a precursor intended for large-scale implementation. The compounds were identified and thoroughly characterized by NMR, LIFDI-MS, FTIR, EA, and SC-XRD. An ALD process using **HeRu31** and O_2 was developed to deposit dense, homogeneous Ru metal thin films at 280 °C with low resistivities. These new precursors show great promise to advance the deposition abilities for Ru and enable the foreseen adaptation of Ru at the smallest levels of ICs.

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9:15am **AF1-TuM-6 Functional Precursor-Driven High-k Atomic Layer Deposition with Improved Throughput and Dielectric Performance**, ***Min Chan Kim**, Seong A Shin, Hae Lin Yang, Jin-Seong Park,* Hanyang University, Korea

With rapid AI advancements intensifying semiconductor demands, interest in high-k dielectrics for logic and memory applications is increasing [1]. High-k materials enable strong gate control with reduced equivalent oxide thickness (EOT), overcoming scaling limitations. Their high dielectric constant primarily arises from strong ionic polarization associated with a narrow bandgap. However, this narrow bandgap lowers the energy barrier for carrier injection, making high-k dielectrics susceptible to increased leakage current. Elevated leakage leads to charge trapping, which degrades threshold voltage stability and overall device reliability [2]. Consequently, suppressing leakage current is essential for practical high-k integration.

In this study, we present a strategy to stabilize high-k dielectric thin films through the incorporation of a functional precursor during film growth. Density functional theory (DFT) calculations reveal that the functional

precursor, introduced between the metal precursor and the reactant, induces a β-hydrogen elimination reaction that selectively removes residual bulky ligands, thereby exposing reactive surface sites and promoting a chemically stabilized growth surface. This ligand removal mechanism is experimentally confirmed by secondary ion mass spectrometry (SIMS), which shows a pronounced reduction in residual carbon and hydrogen species. Importantly, ligand elimination does not result in void formation but instead facilitates the formation of a denser and chemically more stable dielectric film. X-ray photoelectron spectroscopy (XPS) analysis further indicates a reduced oxygen vacancy concentration and an increased metal–oxygen (M–O) bonding ratio, accompanied by increased film density and reduced surface roughness. As a result of this combined chemical and structural stabilization, metal–insulator–metal (MIM) capacitor measurements exhibit a substantial suppression of leakage current and an increase in the dielectric constant. These results demonstrate that functional-precursor-assisted stabilization effectively mitigates leakage-induced reliability degradation while preserving the intrinsic advantages of high-k dielectrics.

Reference

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9:30am **AF1-TuM-7 From Facile Routes for Mid-Valent Molecular Synthons to Vapor Phase Growth of Molybdenum-Based Thin Films***, **Titel Jurca**,* University of Central Florida **INVITED**

ALD technology is established in semiconductor manufacturing and is emerging across broad areas of biotechnology to catalysis. The broad range of substrates, deposition temperatures, and other environmental factors governing the growth and fabrication of this myriad of materials and devices is underpinned by the availability of suitable molecular precursors. Thus, the understanding-based design of novel molecular precursors is pivotal to the continued development of ALD and related vapor phase thin film growth processes (area selective ALD, ALE, CVD). One can envision that a broad range of temperature windows, and ligand chemistries to enable nucleation and subsequent growth are necessary; as well as the design rules to tune those properties on the molecular scale. Currently, the scope of available molecular precursors across the majority of metals of interest is narrow, as is the understanding-based knowledge which governs their design.

For practical reasons, the majority of precursor synthesis often stems from a narrow pool of stable, commercially available, and often fiscally reasonable metal halide precursors. To broaden the pool of ALD precursors, we begin by broadening the pool of accessible metal halide salts; *the precursors to the precursors*. Using stoichiometric silanes, high-valent, mid d-block metal (e.g. Mo, W, Nb, Ta) halides can be controllably, stoichiometrically reduced to highly reactive mid-valent synthons (e.g. $MoCl_3$ from $MoCl_5$). The reactions are facile and produce only H_2 and recoverable and reusable chlorosilanes as byproduct. The resulting mid-valent metal chlorides form ideal starting points towards new precursors for ALD.

From this thrust, we leveraged an $MoCl_3$ synthon to generate the first homoleptic Mo(III)tris-amidinate and guanidinate species. These complexes expand the known scope of tris(amidinate) and tris(guanidinate)M(III) molecules to now include Mo, and add to the very limited knowledge of homoleptic mononuclear Mo(III) coordination complexes. We explore the impact of modifications to the ligand framework, and their implications on synthetic viability, volatility and applicability towards the growth of Mo-based materials by ALD.

ALD Fundamentals: Growth and Characterization
Room HB Plant Ballroom - Session AF2-TuM

Powder ALD

Moderators: Arrelaine Dameron, Forge Nano, **Benjamin Greenberg**, Naval Research Laboratory

10:45am **AF2-TuM-12 ALD on Particulate Materials: Applications & Scale-Up***, **J. Ruud van Ommen**,* Delft University of Technology, Netherlands **INVITED**

Atomic layer deposition (ALD) has been extensively investigated for a wide range of applications and is already used commercially in the semiconductor industry, which predominantly relies on planar substrates. However, the intrinsic ability of ALD to coat nearly any surface geometry with atomic-scale thickness control makes it highly appealing for the coating of particulate materials (particles) as well. Recently, we published a review paper with a quantitative analysis of 799 articles from this field, published from 1988 to 2023 [1]. The obtained dataset is the basis for abstractions regarding reactor types (specifically for particles), coating materials, reactants, supports, and processing conditions. Furthermore, the dataset enables direct access to specific processing conditions.

In this presentation, I will give some examples of ALD on particulate materials we have worked on in my group over the past years, such as pharmaceuticals, batteries, catalysts, and rubber tires. ALD can be used to give pharmaceutical particles delayed-release properties. Battery materials provided with an ALD-made, ultrathin coating have a longer lifetime. This approach of reducing degeneration can also be applied to catalysts, while the island-growth mode can be used to make catalysts in a very controlled way. Finally, replacing carbon black with nanosilica can improve the performance of rubber tires. Treating the nanosilica surface with molecular layer deposition can make it less polar, and enhance the mixing with the rubber during production.

For many of the above applications, it is important to process large amounts of particles, to be able to scale up. Scale-up of ALD on particles is quite different from that on wafers, due to the much larger surface area involved. Proper scale-up of ALD on particulate materials encompasses several aspects, including efficient use of reactants, consistent product quality, and safe operation. I will discuss these aspects, and show some different ways of achieving a large-scale process.

[1] Piechulla, P. M., Chen, M., Goulas, A., Puurunen, R. L., & van Ommen, J. R., Chem. Mater. 38(1) (2026) 20–86.

11:15am **AF2-TuM-14 Temperature-Variation Atomic Layer Deposition: A Strategy for Tuning Particle Size and Dispersion toward High-Performance Catalysts***, Manh Duc Dang, Dieu Minh Nguyen,* Phenikaa University, Viet Nam*; Sri Sharath Kulkarni, J. Ruud van Ommen,* Delft University of Technology, Netherlands*; **Hao Van Bui**,* Phenikaa University, Viet Nam

Precise control over the metal nanoparticle size and dispersion is critical for the synthesis of high-performance catalysts, yet remains challenging due to particle migration and sintering on substrate surfaces. Here, we introduce a temperature-variation atomic layer deposition (TV-ALD) strategy to regulate nucleation and growth of noble metals, demonstrated for the deposition of sub-nanometer Pt on carbon nanopowders by ALD in fluidized bed reactors. By varying the deposition temperature within each ALD cycle, the interplay between the surface chemisorption and the metal species mobility can be manupulated. In particular, the precursor exposure at elevated temperatures ensures efficient chemisorption and nucleation, while the subsequent oxidant exposure at low temperatures suppresses surface diffusion and coalescence of Pt species. This temperature-variation approach enables the formation of highly dispersed Pt species with significantly narrower particle size distributions compared with conventional isothermal ALD processes. Transmission electron microscopy and surface analyses confirm the presence of sub-nanometer Pt clusters with enhanced dispersion across high-surface-area supports. The improved structural control translates directly into enhanced catalytic performance despite a substantially reduced Pt loading. The proposed TV-ALD strategy demonstrates a simple yet powerful process parameter for controlling the nucleation and growth in ALD, providing a scalable pathway toward the synthesis of size-selective noble metal nanoparticles and highly dispersed catalysts.

11:30am **AF2-TuM-15 Achieving Conformality in Fluidized Bed Atomic Layer Deposition on Ultrafine Cohesive Nanopowders**, ***Austin Cendejas,*** *Benjamin Greenberg, Kevin Anderson, James Wollmershauser, Boris Feygelson,* Naval Research Laboratory

Nanoparticles with thin, conformal coatings are of significant interest in a growing number of applications including catalysis, battery technologies, and optoelectronics.[1] Fluidized bed atomic layer deposition (FB-ALD) is a promising technique towards scaling up the batch sizes of these coating processes to industrially relevant scales.[2] A significant challenge emerges as substrate particle size decreases and powders become increasingly "sticky", or cohesive, and persistent agglomeration directly affects the conformality of coatings. In this work we explore several techniques to improve fluidization behavior and ultimately coating conformality of 35 nm diameter Y_2O_3 nanoparticles. Two modes of agitation are explored including vibration and mechanical stirring. Additionally, two coating materials are employed, Al_2O_3 and MgO, providing insight into contributions from precursor molecule size, sticking coefficient, and partial pressure. Each half-cycle of the FB-ALD process is analyzed not only on the reactor scale, but simultaneously on the microscale as persistent porous agglomerates undergo an infiltration-like ALD diffusion-reaction process on the time scale of precursor pulses.[3,4] Quadrupole mass spectrometry is used for in situ diagnostics of reaction progress and both scanning and transmission electron microscopy accompanied by energy dispersive X-ray spectroscopy are used to assess uniformity and conformality of the ALD coatings.

Funding source: NRL base funds, NRC Postdoctoral Fellowship Program

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3. Cendejas, A., D. Moher and E. Thimsen (2020). "Modeling atomic layer deposition process parameters to achieve dense nanocrystal-based nanocomposites." Journal of Vacuum Science & Technology A 39(1).

4. Greenberg, B. L., K. P. Anderson, A. G. Jacobs, A. J. Cendejas, J. R. Hajzus, E. A. Patterson, J. A. Wollmershauser and B. N. Feigelson (2023). "Conformal coating of macroscopic nanoparticle compacts with ZnO via atomic layer deposition." Journal of Vacuum Science & Technology A 42(1).

11:45am **AF2-TuM-16 Atomic Layer DepositionEnabled Control of Densification and Grain Size in ZnO Ceramics**, ***Eric Bissell,*** *Anna Zachariou, Jacob Furst, Steve Lass,* University of Central Florida*; Nicholas G. Rudawski,* University of Florida, Gainesville*; Fernando Uribe-Romo, Titel Jurca, Kathleen Richardson, Romain Gaume, Parag Banerjee,* University of Central Florida

Atomic layer deposition (ALD) provides a versatile approach for applying conformal, nanometer-scale coatings to ceramic nanopowders, offering a means to influence grain-boundary chemistry during sintering. In prior work, ALD Al_2O_3 coatings on ZnO nanoparticles were shown to suppress grain growth;1 however, when consolidated under hot-pressing conditions, this grain growth suppression was accompanied by incomplete densification. These observations motivate a more systematic investigation of how sintering parameters affect densification behavior in ALD-modified powder systems.

In this study, ZnO nanoparticles with an average diameter of 60 nm were coated with 10 cycles of ALD Al_2O_3, corresponding to a nominal coating thickness of ~1 nm, and consolidated by hot pressing using a design of experiments (DOE) approach. The effects of maximum hold temperature (850–1000 °C), applied pressure (25–50 MPa), and hold time at peak temperature (1–120 min) were examined while maintaining identical heating ramps, cooling, and tooling conditions. Eight ceramic samples were produced, spanning a representative subset of the processing space.

The resulting ceramics exhibit systematic variations in relative density and average grain size, indicating that densification behavior remains sensitive to processing conditions despite strong ALD-induced grain growth suppression. This behavior is particularly relevant for transparent ceramic systems, where achieving high density while maintaining sub-wavelength grain sizes is necessary to reduce birefringence- and grain-boundary-related optical scattering. Taken together, these results provide an empirical basis for relating sintering parameters to final microstructure in ALD-coated ZnO systems and illustrate how DOE-based process exploration can inform the development of ALD-enabled ceramics with tunable density and grain size.

Atomic Layer Etching
Room Tampa Bay Salons 3-4 - Session ALE1-TuM
Wet ALE and ALE Modeling

Moderators: Jeffrey W. Elam, Argonne National Laboratory, **Geun Young Yeom**, Sungkyunkwan University

8:00am **ALE1-TuM-1 A Dry-Wet Quasi-ALE Approach for Transition Metals: Tungsten as a Model System**, ***Cinzia Chan,*** KU Leuven and Imec, Italy*; Jean-Francois de Marneffe,* IMEC Belgium*; Christopher Gort,* TU Darmstadt, Germany*; Jill Serron,* IMEC Belgium*; Marta Agati,* IMEC Belgium, Italy*; Felix Seidel,* IMEC Belgium*; Jan P. Hofmann,* TU Darmstadt, Germany*; Stefan De Gendt,* KU Leuven and Imec, Belgium*; Dennis H. van Dorp,* IMEC Belgium, Netherlands **INVITED**

We demonstrate a hybrid dry-wet quasi-atomic layer etching (Q-ALE) process using tungsten as a model case, combining a self-limiting O_2 plasma oxidation (modification) step with a wet-chemical oxide removal step in 1 M HCl. In the study of the modification step, O_2 plasma oxidation was selected for its self-limiting behavior and benchmarked against wet oxidation, which instead produces highly soluble oxides in aqueous solution. The removal step was quantified by ICP-MS, revealing an initially high etch rate that decreases and stabilizes to a background value. This behavior is attributed to the rapid dissolution of plasma-generated bulk WO_3, followed by progressively slower removal as the interface approaches a suboxide-rich layer, and finally a steady-state regime governed by continuous re-oxidation and metal dissolution. Although the background etch rate is very slow (0.03 Å·min^{-1}), in Q-ALE operation the removal step is intentionally stopped before reaching this background regime, enabling controlled and selective material removal. These findings are further supported by post operando XPS, TEM and conductive AFM analyses. The dry-wet Q-ALE sequence was demonstrated on both PVD blanket and ALD-patterned tungsten wafers using existing 300-mm fab tools, achieving ~8 Å per cycle. These results highlight lab-to-fab scalability. More broadly, the combined dry-wet ALE framework provides a versatile platform for layer-by-layer etching of technologically important materials, particularly where purely wet oxidation is not self-limiting (or is chemically challenging), while wet removal offers strong oxide-to-metal selectivity.

8:30am **ALE1-TuM-3 Smooth Post-etch Morphology in Ligand Assisted Molybdenum Wet Atomic Layer Etch**, ***Tulashi Dahal,*** *Trace Hurd, Antonio Rotondaro,* Tokyo Electron America Inc.,

Molybdenum (Mo) has gained significant attention from semiconductor industries for its applications on logic BEOL, buried power rails, and 3 D NAND. Some of these applications require partial etch back of Mo where post-etch morphology is critical to device performance. Wet atomic layer etching offers material removal with Angstrom-level precision at or near room temperature and at ambient pressure by utilizing two sequential self-limiting steps. In the first step, the Mo surface is exposed to an oxidizing solution to form self-limiting surface passivation. In the second step, the modified Mo surface is selectively removed via dissolution in suitable chemistry. Etching of polycrystalline Mo is susceptible to surface roughness increase and uncontrolled etch rate due to solubilization of modified surface products in oxidizing solutions. Here, we present a novel method for controlled Mo etch with improved post-etch surface morphology via ligand assisted surface modification of metallic Mo in aqueous oxidizing solution. A ligand binds with the metal center to form a complex surface product that is insoluble in an aqueous oxidizing solution, preventing the continuous Mo background etch, and resulting in preserved post-etch surface smoothness.

Cyclic etch experiments were carried out by dipping Mo coupons in an oxidizing solution with varying ligand concentration followed by selective removal of modified layer in a low concentration dissolution chemistry. Mo etch rate decreases with increasing ligand concentration. The etch rate, however, can be enhanced via surface oxidation at an elevated temperature (Fig. 1). For the same ligand concentrations, Mo etch rate can be greatly improved by tuning the oxidizer concentration (Fig. 2). A significant enhancement in Mo etch rate [from ~0.12 nm/cycle with p% oxidizer +250 mM ligand to ~0.43 nm/cycle in 5p% oxidizer+250 mM ligand] with increased oxidizer concentrations suggests the formation of thicker surface oxide as surface passivation. For higher oxidizer concentration, Mo ER is independent of ligand concentrations under study (Fig. 2). The measured RMS roughness [~ (0.63±0.04) nm] of the post-etch Mo coupon with higher ligand concentration is the same as RMS roughness of [~ (0.62±0.03) nm] of the reference coupon (Fig. 3). We attribute the preserved morphology in post-etch Mo coupon with higher ligand concentration to the suppression

of continuous Mo etch due to the formation of a stable metal complex that is insoluble in oxidizing solution. The ability to remove Mo at a substantial rate with atomic-level precision and preserved surface morphology in post-etch coupons using less harsh oxidizer and ligand in an aqueous solution near room temperature may provide a cost-effective alternative solution to recess Mo in the industrial scale.

8:45am **ALE1-TuM-4 The Effect of the Angle of Incidence of Ions on Atomic Layer Etching**, ***Joseph Vella,*** TEL Technology Center America*; David Graves,* Princeton University

Plasma assisted atomic-layer etching (ALE) processing techniques have seen widespread usage in the semiconductor manufacturing industry. In its simplest form, an ALE process consists of two steps: a chemical modification step and a removal step. The removal step is often performed by exposing the substrate to a chemically inert plasma (such as an argon plasma) where energetic ions remove the modified surface. In much of the literature, it is assumed that a majority of the ions are hitting the surface at normal incidence, although there are some published results that examine the effect of the ion angle of incidence on ALE behavior. A fundamental understanding of any effect of the ion angle of incidence with in ALE processes is relevant to etching features into patterned surface (especially for high-aspect ratio features). In this work we utilize both classical molecular dynamics (MD) simulations and a reduced order model[1] (ROM) to build this understanding. We focus on the relatively simple case of silicon (Si) ALE by exposure to chlorine gas (Cl_2) and argon ions (Ar^+). We show how the angle of incidence of Ar^+ ions affects the etch per cycle (EPC), etch product distribution, and etch product selectivity.

References

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9:00am **ALE1-TuM-5 Ab Initio Modeling of Atomistic Diffusion of Halogen Species at the Etching Front**, ***Sangheon Lee,*** Ewha Womans University, Republic of Korea

Halogen atoms play key roles in etching processes for semiconducters. Flourocarbon or hydrofluorocarbon gases are commonly used for reactive-ion etching processes. When treated with plasma, these gases decompose and radicals migrate to the etching front. Halogen gases like Cl_2 are often used to treat metal or dielectric surfaces to form halogenated surfaces for atomic layer etching processes. Despite the well-established fact that etching does not proceed without halogen species, detailed surface reaction mechanisms involving halogens are rarely revealed. In this presentation, I will discuss mechanisms of halogen-mediated ethcing processes, focusing on atomistic diffusion of halogen species at dielectric and metal etching fronts. This work is based on state-of-the-art ab initio calculations combined with recent experimental results from my academic colleagues.

9:15am **ALE1-TuM-6 Quantum Chemistry Calculation for Predicting Salt By-Products in ALE Processes**, ***Yuri Barsukov,*** Lam Research Corp.*; Mingmei Wang, Thorsten Lill,* Lam Research Corporation

It is well established that during the thermal and plasma-assisted atomic layer etching of silicon nitride – a process widely used in the semiconductor industry – the main solid by-product is ammonia fluorosilicate (AFS) salt, if the feed gas contains both hydrogen and fluorine. In fact, such chemistries initially convert silicon nitride into AFS salt, which subsequently decomposes into gaseous by-products. During high-aspect ratio etching, the formation of AFS significantly affects the overall process performance by influencing critical characteristics such as etch rate, selectivity, and feature shape distortion, which are vital for semiconductor manufacturing.

Despite this, the thermodynamic properties of AFS – such as its decomposition temperature and the dependence of this temperature on pressure – have not been reliably determined. To address this gap, we performed calculations of standard Gibbs free energies for various crystalline structures of AFS using density functional theory (DFT). The distinctive feature of AFS is that this ionic salt decomposes and sublimates through distortion of ionic bonds, bypassing the liquid state; therefore, DFT level of approach is required to accurately describe such complex chemical bond transformations. The calculations show that the AFS decomposition temperature varies in a wide range depending on its crystal structure and decreases significantly with increasing water content, in agreement with our previous publication [1].

In addition, our simulations show that similar ionic salts with the similar properties – such as NH_4F, NH_5F_2, $(NH_4)_2SiF_6 \cdot NH_4F$, NH_4BCl_3F, $(NH_4)_2TiF_6$, and $(NO)_2SiF_6$ – can also form during etching. These compounds can be classified into reactive and unreactive salts. The simulations predict that some of these salts are stable only at temperatures below 0 ˚C. Given that low-temperature etching is an increasingly important direction in the semiconductor industry, such salts may play a more significant role in future etching processes.

[1] T. Lill *et al.*, "Low-temperature etching of silicon oxide and silicon nitride with hydrogen fluoride," *Journal of Vacuum Science & Technology A*, vol. 42, no. 6, p. 063006, Dec. 2024, doi: 10.1116/6.0004019.

9:30am **ALE1-TuM-7 Influence of Oxide Phase and Surface Facet on Atomic Layer Etching of High-k Metal Oxides**, ***Michael Nolan,*** Tyndall Institute, Ireland*; Rita Mullins,* Tyndall National Institute, University College Cork, Ireland

Thermal Atomic Layer Etching (ALE) is of significant interest for its potential to deliver atomic level control over the etch of many materials, in particular in semiconductor device processing for use in future CMOS nodes with requirements for sub-nm levels of control on complex structures. It is performed using sequential surface modification and volatile release reactions with relevant precursors. For metal oxides, HF is the most widely used modifier. It fluorinates the initial surface to form a metal fluoride layer, leaving the remainder of the film unmodified. The modified, non-volatile layer undergoes ligand-exchange with a second precursors of which TiCl4 and SiCl4 are widely used. This volatilizes the MF4 layer releasing product species. The question of the role of the phase and surface facets in a deposited high-k metal oxide film on thermal ALE has received insufficient attention to date but can be readily addressed with first principles atomistic simulations. In this contribution we use density functional theory simulations to explore the effect of the phase and surfaces of HfO2 and ZrO2 on the HF modification half-cycle of ALE. The models used in this study representing polycrystalline materials are the low energy (111) and (001) surface facets of monoclinic, orthorhombic and tetragonal HfO2 and ZrO2. Our thermodynamic analysis shows that for polycrystalline HfO2 and ZrO2, the HF pulse reacts in a self-limiting manner, and is favoured at temperatures typical of CMOS processing. The upper temperature limit is highly sensitive to the phase and surface of both oxides. Models of HF coverage are used to compute calculated theoretical etch rates for the different oxide phases and surface facets and these show a strong dependence on both the crystal phase and the surface so that if different phases and facets are present in a deposited high-k oxide, an uneven etch profile with increased roughness will be seen. The origin of this dependence arises from the stability, geometry and surface atomic coordination environments in the metal oxides.

9:45am **ALE1-TuM-8 Modeling SiO_2 Atomic Layer Etching Using HF/NH_3 Co-Dosing**, ***Philipp Haslhofer,*** *Tobias Reiter,* TU Wien, Austria*; Alexander Toifl, Andreas Hössinger,* Silvaco Europe Ltd., UK*; Lado Filipovic,* TU Wien, Austria

Atomic Layer Etching (ALE) is a key process for achieving conformal and selective material removal in advanced semiconductor manufacturing, particularly for high-aspect-ratio (HAR) structures in 3D memory and logic devices. Owing to its self-limiting nature, ALE enables uniform etching over extended process times. However, predictive modeling of feature-scale behavior remains challenging due to the interplay of surface modification, diffusion, and volatile etching mechanisms.

In this work, we present a feature-scale simulation framework for cyclic ALE of SiO_2 using HF/NH_3 co-dosing in a chemical-oxide-removal (COR) process. The model is implemented in the in-house process simulator ViennaPS [1] and couples geometry-agnostic Monte Carlo ray tracing for gas-phase transport with a level-set method for surface evolution. During reactant pulses, precursor transport is modeled to be ballistic with cosine angular distributions, appropriate for plasma-less processes. Local surface fluxes obtained from ray tracing are converted into surface concentrations that drive surface reactions. Formation of ammonium fluorosilicate (AFS) is described using a parallel-resistance approach, enabling simultaneous treatment of surface-limited reactions and precursor diffusion-limited reactions through the modified layer. In addition, direct volatile etching of SiO_2 by HF is incorporated via a thickness-dependent coverage function which activates under the conditions of incomplete AFS surface coverage.

Model parameters are calibrated against experimentally reported low-pressure-TEOS thickness data by Hagimoto et al. [2] for planar substrates over a range of precursor pulse times. The calibrated model is subsequently applied to HAR trench structures with aspect ratios up to 20 to investigate the influence of precursor partial pressures and sticking coefficients on etch profiles. The simulations reveal transitions from stoichiometry-limited surface modification to diffusion-limited growth regimes, as well as the

emergence of inverse aspect-ratio-dependent etching under asymmetric HF/NH_3 sticking conditions, highlighting the sensitivity of ALE conformality to surface kinetics. To address the computational cost of simulating large numbers of ALE cycles, we introduce a cycle-skipping strategy in which surface concentrations are recalculated only after several cycles of constant-rate surface propagation. Comparison to gauge simulations, where surface concentrations are reevaluated for each ALE cycle, reveals that up to five cycles can be omitted while maintaining maximum profile deviations below 1% along the surface, corresponding to a significant reduction in computational cost.

Overall, the presented framework provides a physically motivated and geometry-agnostic approach for predictive ALE modeling in HAR structures capturing different reaction pathways and offers insight into the process windows governing conformality, selectivity, and throughput in HAR applications.

Atomic Layer Etching
Room Tampa Bay Salons 3-4 - Session ALE2-TuM
Thermal and Gas-Phase ALE

Moderators: Anil Mane, Argonne National Laboratory, **Fred Roozeboom**, University of Twente

10:45am **ALE2-TuM-12 In Situ ALE/ALD Surface Engineering for Reduced Dielectric Loss in Superconducting Quantum Circuits***, **Neha Mahuli**,* Amazon **INVITED**

Coherence in superconducting quantum circuits is predominantly limited by loss from imperfect surfaces and interfaces, yet atomic layer deposition (ALD) and atomic layer etching (ALE) remain relatively unexplored. In this talk, we present ALD and ALE as a surface-engineering platform for superconducting quantum devices, highlighting performance gains and future opportunities. We describe a post-fabrication, in situ surface treatment integrating ALE and ALD to reduce dielectric loss in aluminum (Al)–based coplanar waveguide (CPW) resonators and transmon qubits on silicon substrates. The process involves conformal removal of native aluminum oxide using thermal ALE at 300°C (trimethylaluminum (TMA) and Hydrogen fluoride(HF)–pyridine chemistry), followed by controlled regrowth of a thin Al2O3 layer using ALD at the same temperature. Surface characterization indicates reduced organic contamination, formation of a thinner Al-rich oxide, and effective cleaning of patterned structures, including metal sidewalls. Applying this treatment to CPW resonators reduces two-level system (TLS) loss at single-photon power by a factor of two. Similarly, for Al transmon qubits, the combined ALE+ALD process increases the mean quality factor by a similar factor, with select devices exceeding 9 x 10^6 million and energy relaxation times above 0.4 ms. Finally, we outline ongoing efforts and some initial results to disentangle the roles of etching and encapsulation, including different ALE chemistries (thermal vs plasma), and in situ ALD of alternative low-loss dielectric capping layers, underscoring the potential of ALD/ALE for surface control in superconducting quantum hardware.

11:15am **ALE2-TuM-14 Fluorine-Free Thermal Atomic Layer Etching of ZrO_2 Using $H_2O/SOCl_2$ Chemistry for Damage-Free Etch-Back of High-k Dielectrics***, **Gyeong Min Jeong**, Jihoon Shin, Jin-Seong Park,* Hanyang University, Republic of Korea

As semiconductor devices continue to scale down, precise dimensional control of individual device components has become increasingly critical. In this context, atomic-scale processing techniques have emerged as key enablers for next-generation semiconductor manufacturing. Among them, thermal atomic layer etching (ALE) has attracted attention as a surface-reaction-driven process capable of removing materials with atomic-layer precision through sequential surface modification and material removal steps. Compared to conventional plasma-based etching, thermal ALE minimizes sputtering-induced damage and effectively suppresses surface roughening. High-k dielectric materials are widely employed as replacements for Si-based insulators in advanced semiconductor devices, enabling sufficient capacitance retention even at deeply scaled technology nodes. However, the dielectric properties of high-k oxides are strongly correlated with their crystalline phases, and achieving ultrathin crystalline films with well-controlled thickness remains challenging. An etch-back approach, in which sufficiently thick crystalline films are first deposited and subsequently thinned while preserving crystallinity, is therefore required. Thermal ALE is well suited for this purpose due to its inherently low-damage characteristics. Most reported thermal ALE processes for high-k materials normally use fluorine-based sources. From this point of view, we propose a novel thermal ALE process for zirconium dioxide (ZrO_2) that does not use the fluorination agent. ZrO_2 films were etched using alternating exposures of H_2O (water) and $SOCl_2$ (thionyl chloride), achieving a self-limiting etch rate of approximately 0.07 Å per cycle. chlorine residues were not detected within the ZrO_2 layer after etching. Surface hydroxylation induced by H_2O exposure forms a reactive termination that facilitates subsequent reactions with $SOCl_2$, enabling continuous and controlled etching. The proposed reaction mechanism is further supported by density functional theory (DFT) calculations. This fluorine-free thermal ALE approach provides precise, damage-free thickness control while preserving the crystalline properties of high-k dielectrics, offering a promising alternative to conventional fluorine-based etching processes for advanced semiconductor manufacturing.

11:30am **ALE2-TuM-15 Thermal Atomic Layer Etching by Halogenation and Ligand-Addition Using N-Heterocyclic Carbenes***, **Aziz Abdulagatov**,* University of Colorado Boulder*; Charles Dezelah, Matthew Surman,* ASM Microchemistry Ltd., Finland*; Steven George,* University of Colorado Boulder

N-heterocyclic carbenes (NHCs) are strong electron pair donors and can bind to metal centers by ligand-addition.In this study, etching of Al_2O_3 was demonstrated using halogenation with hydrofluoric acid (HF) followed by ligand-addition using NHCs.The NHC sources were 1,3-dimethylimidazolium-2-carboxylate ($IMeCO_2$) or 1,3-di-tert-butylimidazol-2-ylidene (ItBu) (**Figure 1**).The thermal ALE of Au and Co was also demonstrated using hydrochloric acid (HCl) together with $IMeCO_2$ or ItBu.The studies were conducted using in situ quartz crystal microbalance (QCM) measurements.

Al_2O_3 thermal ALE was achieved using sequential HF and $IMeCO_2$ or ItBu exposures at temperatures from 230 to 290 °C.QCM profiles showed a self-limiting mass gain during fluorination and a self-limiting mass loss during the NHC ligand-addition step (**Figure 2a**).The mass change per cycle yielded an etch rate of 3.3 Å per cycle at 290 °C. The spontaneous etching of Al_2O_3 films was also observed during exposure to 2,2-difluoro-1,3-dimethylimidazolidine (DFI) (**Figure 1**).DFI provides both fluorination and ligand-addition by the NHC remaining after fluorination.DFI leads to continuous Al_2O_3 spontaneous etching at 200 to 270 °C.

The NHCs were also effective for Au and Co thermal ALE.Sequential exposures of HCl and $IMeCO_2$ or ItBu led to a linear mass decrease with the number of ALE cycles. The maximum Au mass change yielded an etch rate of 0.83 Å per cycle at 250 °C using HCl and $IMeCO_2$ (**Figure 2b**). For Co, the maximum etch rate was 3.0 Å per cycle at 290 °C using HCl and ItBu. These ALE processes are believed to proceed through the formation of volatile metal chloride–carbene adducts.The cycle times during Au and Co ALE were much shorter than earlier cycle times for Au and Co ALE measured using phosphines for ligand-addition.

11:45am **ALE2-TuM-16 Influence of Fluorination and Oxygenation Sources on the Thermal Atomic Layer Etching of MoS_2***, **Spencer P. Smith**, Jacob A. Tenorio, Icelene Leong, John D. Hues, Steven M. Hues, Elton Graugnard,* Boise State University

Atomic layer etching (ALE) has proven to be a transformative technique for atomic scale processing of two-dimensional (2D) materials, including molybdenum disulfide (MoS_2), a promising material in the semiconductor industry because of its high mobility in its monolayer form. Precise etching of MoS_2 films can offer a route to desired electrical and optical properties through controlling film thickness. Previous research reported MoF_6 and H_2O as precursors for thermal ALE of MoS_2. Here, we report on progress with alternative fluorination and oxygenation sources and assess their effectiveness of thermal ALE of MoS_2. Oxygen sources include H_2O and O_3, and fluorine sources include HF/Pyridine and MoF_6. Etch rates, uniformity, and surface chemistry following ALE were characterized through spectroscopic ellipsometry, atomic force microscopy, Raman spectroscopy, and X-ray photoelectron spectroscopy. The results of ALE of amorphous MoS_2 with HF indicated that there were no signs of etching with H_2O at 200 °C or 300 °C. ALE with HF and O_3 produced a mass loss per cycle of 25 ng/cm^2 at 200 °C and an etch per cycle (EPC) of 0.4 Å, similar to prior results of 0.5 Å/cyc with MoF_6 and H_2O. However, MoF_6 with O_3 at 200 °C on amorphous MoS_2 films exhibited non-self-limiting etch behavior with a mass loss per cycle of 126 ng/cm^2. Lowering the temperature to 150 °C resulted in self-limiting ALE with a mass loss per cycle of 63 ng/cm^2. Although surface oxygen concentrations increased from etching, surface morphology showed little change on amorphous films. Results for application of these chemistries to crystalline MoS_2 films will be discussed.

This research further broadens the capabilities of atomic layer etching for precise processing of 2D materials.

Emerging Materials and Processes
Room Tampa Bay Salons 1-2 - Session EM1-TuM
Molecular Layer Deposition/Hybrid ALD

Moderators: Haripin Chandra, The Electronics business of Merck KGaA Darmstadt, **Keith Wong**, Applied Materials

8:00am **EM1-TuM-1 ALD Outstanding Presentation Award Finalist: The Impacts of Organic Structures on the Sensitivity of Molecular Atomic Layer Deposited EUV Resist Thin Films***, Thi Thu Huong Chu, Dan Le,* University of Texas at Dallas*; Markus Langer, Gregrey Swieca,* University of Mississippi*; Doo San Kim, Minjong Lee, Dushyant Narayan,* University of Texas at Dallas*; Nikhil Tiwale,* Brookhaven National Laboratory*; Jean-Francois Veyan,* University of Texas at Dallas*; Michael Eller,* University of Mississippi*; Chang-Yong Nam,* Brookhaven National Laboratory*;* ***Jiyoung Kim****,* University of Texas at Dallas

Until now, the development of advanced hybrid EUV resists has largely emphasized inorganic metals with high EUV absorption, while the contribution of organic components remains insufficiently explored. In this work, we investigate how organic backbone structures influence the sensitivity and patterning performance of EUV resist materials, focusing on resist thin films synthesized via molecular atomic layer deposition (MALD) for next-generation EUV lithography. Under EUV exposure, negative tone MALD resist thin films consistently show that organic moieties with an aliphatic chain-based backbone exhibit enhanced sensitivity and improved patterning performance compared with those featuring an aromatic backbone.

To elucidate the underlying mechanisms responsible for the observed enhancement, various material characterization techniques, including in situ FTIR, XPS, Raman, and NP-SIMS, were conducted for two Zn-based systems that feature either organic with an aliphatic chain backbone [e.g., 2,3-dimercapto-1-propanol (DMP)], or an aromatic backbone [e.g., 4-mercaptophenol (4-MP)]. IR measurements, obtained from the in-situ FTIR system equipped with an electron flood gun, indicate clear changes in the aromatic ring of 4 MP upon electron exposure, reflected by a decrease in C=C bond. Additional material characterizations further confirm the changes in the aromatic ring and suggest the formation of graphitic-like carbon within 4-MP-based resist materials upon electron exposures. In contrast, while IR measurements of DMP-based resist thin films show evidence of new species formation, as indicated by an increase in various carbon species, NP-SIMS suggests changes in the oxidation state of Zn within DMP-based resist thin films.

Based on these material characterizations, we propose two distinct exposure mechanisms that potentially govern the sensitivity and patterning behavior of Zn/4-MP and Zn/DMP resist thin films. For the aromatic-based system, the organic moiety likely undergoes crosslinking, leading to the formation of a graphitic-like carbon network, whereas the aliphatic chain–based organic forms complex structures with the metal core surrounded by ligands. These findings provide critical guidance for the molecular design of MALD EUV resist thin films, enabling a balance between sensitivity and pattern fidelity to meet next-generation lithography performance targets.

This work is supported by the U.S. DOE Office of Science Accelerate Initiative Award 2023-BNL-NC033-Fund. This research is also partially supported by the National R&D program (2022M3H4A3052556) through the National Research Foundation of Korea (NRF), funded by the Ministry of Science and ICT in Korea.

8:30am **EM1-TuM-3** ***All-Dry-Processed*** **Zn-Based Inorganic–Organic Hybrid Photoresists for EUV Lithography***, Thi Thu Huong Chu, Dan N. Le, Dushyant M. Narayan, Minjong Lee, Doo San Kim,* University of Texas at Dallas*; Nikhil Tiwale, Chang-Yong Nam,* Brookhaven National Laboratory*; Jiyoung Kim,* University of Texas at Dallas

Extreme ultraviolet (EUV) lithography is the key enabling technology for sub-10 nm metal half-pitch semiconductor nodes.[1] However, one of the primary bottlenecks lies in the development step of the lithography process. Conventional wet development often leads to pattern collapse due to capillary forces generated during solvent evaporation.[2,3] Although this issue is less severe in high- and hyper-NA EUV lithography as a result of reduced resist thickness, wet development can still degrade pattern fidelity through solvent-induced swelling, non-uniform dissolution, and surface-tension-driven stochastic effects, thereby increasing LER and defectivity.

To address these challenges, dry development processes are emerging as a promising alternative, eliminating the patterning issues associated with wet developers and their associated environmental costs. Here, we present a dry development approach of the Zn-based hybrid inorganic–organic resist systems deposited by molecular layer deposition (MLD). The resist films were patterned using both low-energy electron-beam lithography (100 V EBL) and EUVL. Dry development was then carried out by chemical vapor exposure to hexafluoroacetylacetone (hfacH), which reacts with the Zn-based resists, generating volatile products such as $Zn(hfac)_2$ and organic by-products. During wet development, resist–developer interactions cause lift-off problems that hinder accurate sensitivity evaluation, and high-resolution patterning is degraded by resist swelling and spreading. In contrast, the dry development process achieves a tenfold improvement in sensitivity over wet development while resolving features as small as 10 nm with EUVL. This demonstrates the strong resistance of the exposed regions to hfacH vapor and the elimination of capillary-induced collapse, enabling controlled material removal without the limitations of liquid immersion. Among currently reported all-dry-processed EUV resists, we achieved a low critical dose of 27 mJ/cm^2 with a comparable LER of 1.6 nm.

These findings demonstrate a significant step toward realizing an all-dry EUV resist platform. By combining MLD-based hybrid resist materials with vapor-phase development, this approach not only mitigates fundamental limitations of wet processing but also opens pathways for scalable, high-performance patterning required for next-generation semiconductor manufacturing.

This work is supported by the U.S. DOE Office of Science Accelerate Initiative Award 2023-BNL-NC033-Fund. This research is also partially supported by the National R&D program (2022M3H4A3052556) through the National Research Foundation of Korea (NRF), funded by the Ministry of Science and ICT in Korea.

[1] I. Giannopoulos *et al.,* Nanoscale, **2024**, 16, 15533–15543.

[2] T. S. Kulmala *et al.,* Proc. SPIE, **2016**, 9776, 97762N.

[3] N. Kenane *et al.,* J. Photopolym. Sci. Technol., **2024**, 37, 257–262.

8:45am **EM1-TuM-4 Polyurea Molecular Layer Deposition using Low Melting Point Precursors for Use in Biosensor Design***, Jay Werner, Seancarlos Gonzalez,* ***David Bergsman****,* University of Washington

Molecular layer deposition (MLD) is a promising tool that can take the place of silane-based SAMs in some surface functionalization applications where a multilayer film is acceptable and a precise, conformal film thickness is desirable, such as in biosensor design. However, many organic MLD precursors have low vapor pressure or are solids at room temperature, which can lead to increased purge times and the possibility of condensation-induced valve clogging. This work presents an underexplored polyurea MLD chemistry using 2,4-toluene diisocyanate (TDIC) and ethylene diamine (ED).This process has some benefits over the similar and more common 1,4-phenylene diisocyanate (PDIC) reactant, such as reduced cost and lower melting point (and thus higher vapor pressure at room temperature). Film characterization suggests that this process is similarly well-behaved to PDIC-based polyurea: in situ ellipsometry shows that the process is both linear up to 55 cycles and self-saturating, XPS analysis shows the expected atomic ratio of oxygen and nitrogen in the film, and FTIR shows amide I & II peaks characteristic of polyurea. In addition, the films were analyzed using zeta potential analysis, fluorescence tagging, and water contact angle (WCA) goniometry to characterize their suitability for use in biosensor design.

9:00am **EM1-TuM-5 Conformality of Molecular Layer Deposited Polyurea for Sidewall Passivation***, Wallis Scholl,* Colorado School of Mines*; Thorsten Lill, Mingmei Wang, Wenyu Zhang, Louis Kim, Harmeet Singh,* Lam Research Corporation*; Sumit Agarwal,* Colorado School of Mines

As the semiconductor industry transitions from fluorocarbon plasma chemistries to carbon-free reactive plasmas, new techniques are needed to passivate the sidewalls of high aspect-ratio (HAR) features during etch. Molecular layer deposition (MLD) is a vapor-phase thin film growth technique comprised of alternating surface reactions for deposition of organic and hybrid organic-inorganic chemistries. While MLD is an analogous technique to atomic layer deposition (ALD), the growth mechanism of MLD has added complexity due to the possibility of double reaction of both functional groups in the precursor molecule with the growth surface and physisorption of molecules into the film. Previous work on ALD has found that conformal deposition on HAR features requires very high precursor doses to supply necessary diffusive flow. However, we have

found that MLD polyurea films are surprisingly conformal using the saturation doses for a flat surface.

Polyurea was deposited via MLD using toluene diisocyanate and ethylene diamine as precursors. Figure 1 a) and b) shows scanning electron microscopy (SEM) images of AR~65:1 holes in SiO_2-SiN_x stacks, both with and without ~10 nm of polyurea deposited via MLD. The chips were then exposed to an etching plasma and imaged again [see Figure 1 c) and d)], and the presence of polyurea was found to result in a smaller CD throughout the entire feature. This result shows that during MLD, polyurea was deposited throughout the entire hole and then was able to protect the sidewalls during etch. We have attributed the unexpectedly high conformality of MLD to the physisorption contribution to film growth which we have shown in detail in previous work. This physisorbed material is free to diffuse throughout the film, which may assist in deposition at the bottom of the hole. However, the process must be carefully designed with this effect in mind, as physisorbed molecules can also diffuse out of the film, resulting in chemical vapor deposition when precursor molecules react in the gas phase. Further, we have studied the plasma-surface interactions of polyurea with HF plasma and shown that polyurea can act as a sacrificial layer during HF etch. When polyurea was deposited on top of SiO_2 or SiN_x and then exposed to an HF plasma, only the polyurea film was etched during initial plasma exposure, while the underlying material was protected. Only once the polyurea was completely consumed by reaction was SiO_2/SiN_x etch observed (see Figure 2). This work presents a new technique for sidewall passivation during HF etch.

9:15am **EM1-TuM-6 Molecular Layer Deposition of Polyamide Membranes for Selective Water and Ion Transport**, ***Ruoke Cai***, 21 Kiryat Technion, Israel; *Brian Welch, Aleksandr Ershov, Jay P. Singh,* Technion Israel Institute of Technology, Israel; *Jeremiah W. Woodcock, Christopher Stafford,* NIST; *Kirti Sankhala,* Indian Institute of Technology Jodhpur, India; *Guy Ramon, Razi Epsztein, Viatcheslav Freger, Tamar Segal-Peretz,* Technion Israel Institute of Technology, Israel

Molecular Layer Deposition (MLD) offers atomic-scale precision for fabricating organic and hybrid materials, yet its applications in membrane technology remains relatively underexplored. Nanofiltration (NF) and reverse osmosis (RO) are critical techniques in desalination and water treatment, addressing the growing challenges of water scarcity. Conventional interfacial polymerization replies on rapid, diffusion limited reactions that produce structurally heterogeneity, and presence of sub-nanometer defects that limit membrane selectivity.

Here, we explore MLD as a new platform for fabricating polyamide-based filtration membranes, utilizing MLD precision for creating homogenous, defect-free high-performance filtration membranes. MLD RO membrane with an optimized thickness of 12 nm exhibited a twofold improvement in H_2O/NaCl selectivity compared to commercial desalination membranes. In addition, the defect-free nature of these membranes further enables probing the intrinsic properties of polyamide. MLD NF membrane display narrow effective pore size distributions and pronounced monovalent-divalent ion discrimination in both cation (Li^+/Mg^{2+}) and anion (Cl^-/SO_4^{2-}) separations. Overall, this work establishes MLD as versatile platform for fabricating angstrom-precise polyamide membrane, providing new opportunities to design next-generation filtration membranes for advanced water and ion transport.

9:30am **EM1-TuM-7 Cyclic Siloxane Precursor for Molecular Layer Deposition of Polymer Networks**, ***Sanne Deijkers***, *Peter Gordon, Seán Barry,* Carleton University, Canada

Phosphane-ene polymer networks, typically made in bulk phase synthesis, are known for their oxygen scavenging properties, making them ideal as protective layers. Molecular layer deposition (MLD) of polymer networks offers the opportunity to engineer thin film polymer networks for flexible electronics, sensors, and other applications. MLD of phosphane-ene was demonstrated using the cyclic siloxane precursor tetramethyltetravinylcyclotetrasiloxane (D_4^{Vinyl}), isobutylphosphine (iBuPH$_2$), and an Ar plasma to generate P radicals to act as a cross-linking agent [1]. The D_4^{Vinyl} ring can remain intact and improve crosslinking in the MLD film, which is what our group proposed what happens during the phosphane-ene MLD process [1], while the Knez group suggested ring opening in their work on MLD of siloxane-alumina films [2,3] . In this work, various growth mechanisms of polymer networks using the cyclic D_4^{Vinyl} precursor have been studied.

It was found that a long-lived radical is crucial to provide cross-linking. Switching from the primary phosphine iBuPH$_2$ to a primary amine tBuNH$_2$ did not result in growth. *In situ* quartz crystal microbalance (QCM) displayed pulsing of the precursors, but no mass gain was observed. The short-lived N radical proved to be unsuitable for MLD of polymer networks through radical-mediated cross-linking.

The deposition reaction mechanisms of phosphane-ene MLD were examined. *In situ* cycle-by-cycle QCM was combined with *ex situ* ellipsometry, atomic force microscopy, and Fourier transform infrared spectroscopy. Together, it can be hypothesized that the reaction mechanism of D_4^{Vinyl} is dependent on the surface chemistry. The presence of a radical species versus a metal atom at the surface decides the favorability of ring-opening, with the π-acid nature of the metal playing a significant role in ring opening. This presentation will detail different mechanisms using the D_4^{Vinyl} precursor and discuss its implications on film density.

[1] J. T. Lomax *et al.*, *Chem. Mater.*, 35, 4, 2023

[2] K. Ashurbekova *et al.*, *Chem. Mater.*, 33, 3, 2021

[3] K. Ashurbekova *et al., Chem. Commun.*, 57, 17, 2021

9:45am **EM1-TuM-8 Extreme Ultraviolet and Electron Beam-Induced Decarboxylation of Hybrid MLD Aluminum Oxalate Photoresists**, ***Long Viet Than***, Stanford University; *Miso Kim,* Hongik University, Republic of Korea; *Oleg Kostko,* Lawrence Berkeley National Laboratory (LBNL); *Bonggeun Shong,* Hongik University, Republic of Korea; *Stacey F Bent,* Stanford University

Continued device scaling with the introduction of high numerical aperture (NA) extreme ultraviolet (EUV) lithography will require innovations in photoresist materials. Particularly, new resist chemistries are needed to address the photon and material stochastics challenges that define the current resolution limit. Molecular layer deposited (MLD) metal-organic photoresists offer intrinsic advantages in precise thickness control and chemical homogeneity that can address some of these challenges. However, many MLD resists have poor EUV and electron beam sensitivity, leading to the need to explore new molecular designs that better harness the reactions induced by EUV-generated electrons.

In this work, we introduce a rationally designed MLD resist utilizing metal carboxylate groups to provide an efficient solubility switch mechanism by using trimethylaluminum (TMA) and oxalic acid precursors to deposit aluminum oxalate thin films. X-ray photoelectron spectroscopy (XPS) and infrared spectroscopy reveal their chemical structure, showing that the metal oxalate coordination network reorganizes during exposure to air. We investigate the resist patterning mechanism and performance via electron beam lithography and flood EUV exposure. We use XPS and atomic force microscopy (AFM) to study post-e-beam chemical changes and film shrinkage, and in situ residual gas analysis and total electron yield measurements to identify reactions occurring during EUV exposure. Results show that exposure-induced decarboxylation results in CO/CO_2 gas evolution, inorganic Al-O bonding, and negative tone patterning. The photoresist can be developed with water, yielding an e-beam sensitivity of ~8500 μC/cm^2 (at 100 keV accelerating voltage) and EUV sensitivity of ~200 mJ/cm^2 – among the best for Al-based resists in the literature. Using electron beam lithography, line/space patterns as small as 14 nm half pitch are resolvable, with a line width roughness (LWR) of 5.2 nm. Thus, this work provides a new chemical motif applicable to hybrid MLD photoresists and highlights the importance of the organic ligand in determining the efficiency of the patterning mechanism.

Emerging Materials and Processes
Room Tampa Bay Salons 1-2 - Session EM2-TuM

Vapor Phase Infiltration

Moderators: Jiyoung Kim, University of Texas at Dallas, **Il-Kwon Oh**, Ajou University

11:00am **EM2-TuM-13 Vapor Phase Infiltration as a Route to Precise Atom Number Cluster Synthesis and Cation Substitution**, *Kihoon Kim, Nuwanthaka Jayaweera, Taylor Harville, Cong Liu,* ***Alex Martinson***, Argonne National Laboratory

The energetically favorable formation of atomically precise clusters enables nanoscale synthesis with exquisite uniformity. We report the synthesis of InS- and CdS-core clusters via vapor infiltration of atomic layer deposition precursors directly into polymer thin films. Sequential infiltration of trimethylindium vapor and hydrogen sulfide gas into poly(methyl methacrylate) (PMMA) allows growth of clusters uniform properties consistent with a magic size cluster–$In_6S_6(CH_3)_6$. Most recently we demonstrate that post-synthetic vapor phase cation substitution into InS-

core clusters as deposited in the polymer film is possible for a limited number of ALD precursors, consistent with DFT modeling. Gas phase dimethyl cadmium and hydrogen sulfide precursors infiltrated into poly(4-vinylpyridine) thin films also results in the 3D-nucleation of clusters consistent with a cubane-type Cd_4S_4 core with variable ligand capping. Most recently, we have utilized in situ UV/visible reflection/absorption spectroscopy to observe in real-time the nucleation and growth of CdS clusters for greater mechanistic insight, further supported by DFT. Together the novel approach and in situ characterization methods allow access to and insight into cluster syntheses previous restricted to the solution phase, with the added benefits of rapid byproduct elimination through purging under low vacuum as well as avoidance of the purification, concentration, and film casting required for solution phase cluster syntheses.

11:15am **EM2-TuM-14 Activated Direct Reaction between Carbonyl Groups in Poly(Methyl Methacrylate) (PMMA) and Diethylzinc (DEZ) During Vapor-Phase Infiltration***, Nikhil Tiwale,* Brookhaven National Laboratory*; Ashwanth Subramanian, Sayantani Sikder,* Stony Brook University*; Xiaohui Qu, Guillaume Freychet,* Brookhaven National Laboratory*; Eliot Gann, Cherno Jaye,* National Institute of Standard and Technology*; Kim Kisslinger, Jorge Anibal Boscoboinik,* ***Chang-Yong Nam****,* Brookhaven National Laboratory

Vapor-phase infiltration (VPI) enables organic–inorganic hybrid materials by allowing organometallic precursors to diffuse into polymer matrices and react with specific functional groups. In poly(methyl methacrylate) (PMMA), infiltration using highly reactive trimethylaluminum (TMA) is well established, whereas diethylzinc (DEZ) is generally considered insufficiently reactive toward PMMA carbonyl groups and therefore requires alumina priming. The prevailing model assumes that ZnO_x growth proceeds exclusively through reactions between DEZ and hydroxyl groups generated during the AlO_x priming step.Here, we show that alumina priming directly activates neighboring carbonyl groups in PMMA, enabling a previously unrecognized, direct reaction pathway between DEZ and the polymer backbone during VPI [1]. Using in situ quartz crystal microbalance measurements, cross-sectional scanning transmission electron microscopy, infrared reflection-absorption spectroscopy (IRRAS), near-edge X-ray absorption fine structure (NEXAFS) spectroscopy, and density functional theory (DFT) simulations, we elucidate the mechanism responsible for accelerated ZnO_x infiltration in AlO_x-primed PMMA.AlO_x infiltration rapidly saturates due to near-surface free-volume clogging caused by hyperbranched AlO_x network formation, whereas ZnO_x infiltration exhibits increasing mass uptake and deeper, more uniform penetration over successive cycles. Spectroscopic analyses reveal progressive carbonyl consumption during ZnO_x cycles and the emergence of formate-like species, inconsistent with a hydroxyl-only mechanism. DFT calculations support the formation of a stabilized cyclic Zn-Al-O adduct involving an AlO_x-activated carbonyl group, which lowers the energetic barrier for DEZ binding.These results establish a revised mechanistic framework in which alumina priming electronically activates polymer functional groups, enabling direct DEZ-carbonyl reactions and sustained ZnO_x infiltration, with implications for the design of high-fidelity infiltration-based hybrid materials.

[1] N. Tiwale et al., *Chem. Mater.*, in press (2026), https://doi.org/10.1021/acs.chemmater.5c02584

11:30am **EM2-TuM-15 Atomic Layer Processes for UV-Stable Polymers: Synergistic Effects of Infiltration and Deposition of ZnO***, Gil Menasherov, Nidaa S. Herzallh, Tamar Segal-Peretz,* Technion Israel Institute of Technology, Israel

Ultraviolet (UV) radiation is the major cause for polymer degradation in outdoor environments, accelerating mechanical failure and color change, leading to plastic waste accumulation. Effective UV-protective strategies that preserve polymer functionality are therefore critical for extending material longevity in UV-intense environments. Here, we present a synergistic approach combining vapor phase infiltration (VPI) and atomic layer deposition (ALD) to engineer nanoscale zinc oxide (ZnO) coatings on poly(lactic acid) (PLA), a UV-sensitive polymer. Individually, ALD and VPI offer minimal enhancement in UV stability; however, their sequential application enables the formation of conformal, polycrystalline ZnO films that dramatically improve UV resistance in both 3D-printed structures and thin-film PLA models. In situ microgravimetry and cross-sectional electron microscopy reveal that VPI introduces ZnO nucleation sites within and atop the polymer matrix, promoting a >10-fold increase in ZnO growth per ALD cycle. The resulting ZnO–PLA hybrids absorb over 90% of incident UV-C radiation while maintaining high optical transparency in the visible range. This low-temperature, scalable process provides a promising platform for the development of transparent, durable UV-barrier coatings on polymers for use in environmentally demanding applications.

11:45am **EM2-TuM-16 Vapor Phase Infiltration of ZnO Nanocrystals into Biodegradable Fibers for Dermatologic Applications***, Martina Rihova,* CEITEC Brno University of Technology, Czechia*; Susan Azpeitia,* CIC nanoGUNE, Spain*; Denisa Fenclova, Zbynek Heger,* Mendel University in Brno, Czechia*; Mato Knez,* CIC nanoGUNE; IKERBASQUE, Basque Foundation for Science, Spain*; Jan Macak,* CEMNAT, University of Pardubice; CEITEC Brno University of Technology, Czechia

Vapor Phase Infiltration (VPI) enables the incorporation of metal oxides into polymer materials (1,2). Among other applications, allows the development of active antibacterial polymer-inorganic composites (3,4) and photocatalysts (5).

In this study, VPI was used to infiltrate polyvinyl alcohol or cellulose acetate (CA) fibers with ZnO for the treatment of *Acne vulgaris*. The fibers were prepared from biodegradable polymers using an innovative centrifugal spinning technique (6) and subsequently subjected to VPI using diethyl zinc and water, leading to the formation of ZnO both within the fibers and on the fiber surfaces. (3,4)

The fibers were infiltrated with ZnO via VPI using 1 to 128 cycles. Since ZnO-infiltrated CA fibers do not release ZnO nanocrystals, these fibers were treated with oxygen plasma to modify their solubility (4) The resulting fibers with infiltrated ZnO nanocrystals were comprehensively characterized using SEM, TEM, XRD, and XPS. Antibacterial testing revealed that both CA and PVA fibers infiltrated with ZnO nanocrystals starting from 32 VPI cycles effectively inhibited the growth of acne-causing bacteria. Moreover, the homogeneous distribution of ZnO nanocrystals within the fibers enabled the immediate release of Zn^{2+} ions while preserving the fibrous structure, in contrast to fibers containing ZnO nanoparticles, which directly blended into the spinning solution. (3,4)

The presenation will demonstrate that fibrous carriers combined with active ZnO nanocrystals prepared via VPI represent a highly promising material, showing significant potential for the treatment of *Acne vulgaris*.

References:

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3 Rihova et al. "Centrifugally spun and ZnO-infiltrated PVA fibers with antibacterial activity for treatment of Acne vulgaris." *Journal of Controlled Release* (2025): 113777.

4. Rihova et al."Cellulose Acetate Fibers with Infiltrated ZnO Nanocrystals: Activation of Antibacterial Properties against *Acne vulgaris* by Oxygen Plasma Treatment" *Small*, Ms submitted.

5. Chennam et al. "Carbon fibers with infiltrated TiO2 nanocrystalline layers: photocatalytic performance." *Nanoscale* (2026).

6. Hromadko et al. "Nanofibers: where they are where we need them to be." *Frontiers in Nanotechnology* 7 (2025): 1706183.

ALD Applications

Room Ybor Salons I-IV - Session AA1-TuA

ALD for Catalysts and Fuel Cells

Moderators: Hao Van Bui, Phenikaa University, **Nathanaelle Schneider**, CNRS-IPVF

1:30pm **AA1-TuA-1 Copper's Cosy Blanket: A Comparison of Non-Selective and Area-Selective ZnO deposition on Catalyst Stability**, ***Kalani Ostermeijer***, *Ruud van Ommen, Evgeny Pidko,* Delft University of Technology, Netherlands

In the past few decades, valorizing CO_2 has drawn significant interest as it offers a more carbon neutral pathway to chemicals and fuels. However, CO_2 reduction has proven to be problematic due to its thermodynamic and kinetic constraints. Heterogeneous thermo-catalysts can improve the kinetics, thus play a critical role in the push for the industrialization of sustainable chemicals and fuels. Methanol is considered a promising product thanks to being a key chemical building block. Currently, the commercial $Cu/ZnO/Al_2O_3$ catalyst requires harsh conditions (50-100 bar H_2 and 200-300 °C). After prolonged exposure to temperatures above 200 °C, sintering of the dispersed active phase is observed. This was shown to worsen in the presence of water vapor, which is produced in high amounts during the hydrogenation process. Therefore, protecting Cu nanoparticles from thermal and hydrothermal sintering is key to enhancing the operating productivity and efficiency of the methanol production process.

In this work we aim to protect Cu nanoparticles by forming a ZnO overlayer on top of a Cu/SiO_2 catalyst using both non-selective and area-selective atomic layer deposition. ZnO was deposited using diethyl zinc and ethanol under atmospheric pressure in a fluidized bed reactor at 100 °C. To induce area-selectivity, the Cu/SiO2 catalyst was treated with trimethoxypropylsilanes using air-free wet synthesis techniques, passivating surface silanol groups. All catalysts were characterized using temperature programmed desorption, elemental analysis, electron microscopy (focused ion beam scanning electron microscopy and transmission electron microscopy), and x-ray photoelectron spectroscopy, and their stability was assessed in a fixed-bed reactor under industrially relevant conditions (250 °C and 50 bar). Herein, we explore how tailoring the metal oxide interface using targeted ZnO deposition can alter the stability of Cu/ZnO based methanol hydrogenation catalysts, improving the rational design of catalysts via ALD.

This work is part of the Advanced Research Center for Chemical Building Blocks, ARC CBBC, which is co-founded and co-financed by the Dutch Research Council (NWO) and the Netherlands Ministry of Economic Affairs and Climate Policy

1:45pm **AA1-TuA-2 Effect of Buffer Layers on Cobalt-Based Thin-Film Catalysts for Fischer–Tropsch Synthesis**, ***Muhammad Hamid Raza***, *Avela Kunene,* Helmholtz-Zentrum Berlin (HZB), Germany*; Lucia M. Toscani,* Department of Interface Design, HZB, Germany*; Alexander Steigert,* Helmholtz-Zentrum Berlin (HZB), Germany*; Athanasios Skaltsogiannis,* Department of Interface Design, HZB, Germany*; Ali Shan Malik,* Helmholtz-Zentrum Berlin (HZB), Germany*; Catalina E. Jiménez,* Department Interface Design, HZB, Germany*; Marcus Bär,* Department of Interface Design and Energy Materials In-Situ Laboratory Berlin (EMIL), HZB, Berlin. Helmholtz-Institute Erlangen-Nürnberg for Renewable Energy (HI ERN), Berlin. Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU), Erlangen., Germany*; Rutger Schlatmann, Daniel Amkreutz,* Helmholtz-Zentrum Berlin (HZB), Germany

In Fischer-Tropsch synthesis, *hcp*-Co^0 nanoparticles show higher CO dissociation activity and enhanced C_{5+} selectivity than the *fcc*-Co^0 nanoparticles due to the presence of more numerous and more active B_5 sites.[1] As such, thin film catalysis offers opportunities to tailor catalysts properties by design that are pre-adapted to specific crystallographic morphology for their targeted application. Fischer-Tropsch synthesis (FTS) benefits from thin film catalysts, by selectively tailoring the catalytically most active phase *i.e., hcp*-Co^0. This streamlined catalyst design enhances catalytic activity and selectivity toward the desired end products.[2] Varying deposition conditions and metal-support interactions affect the reducibility and crystallographic morphology of the FTS active phase. Herein, cobalt-based thin film FT catalysts are synthesized with varying chemical structures and crystallographic phases, including metallic and metal oxides phases, onto various supports and buffer layers (Al_2O_3, SiO_2, ZrO_2, CeO_2, Si_xN_y, Si_xC_y, TiO_2). Key properties such as film morphology and stability, as well as metal/metal oxide–support interactions (MSI) in terms of support-induced reducibility and morphological evolution of the cobalt films are investigated in thin films catalyst systems. Phase changes are systematically studied under *in-situ* FTS-relevant oxidation–reduction conditions using synchrotron grazing incident X-ray diffraction. Indeed, as-deposited metallic cobalt shows higher stability than its oxide counterpart, the *spinel*-Co_3O_4, under FT-relevant reduction conditions. A semi-quantitative analysis of the diffraction data indicates that the relative *fcc*-to-*hcp* ratio depends on the nature of the buffer layer, with samples supported on CeO_2, TiO_2 and Al_2O_3 - SiO_2 exhibiting the lowest apparent *fcc*/*hcp* ratio. These well-defined cobalt-based (Co, Co_xO_y) thin film catalysts offer a promising alternative for enhancing FT performance. Clear structure–property correlations will be presented to guide the rational design of advanced FT catalyst systems.

1 Liu, J.-X., Wang, P., Xu, W. & Hensen, E. J. M. Particle Size and Crystal Phase Effects in Fischer-Tropsch Catalysts. *Engineering* **3**, 467-476 (2017).

2 Kunene, A. *et al.* Thin-Film Catalysis Innovations in Fischer–Tropsch Synthesis for Enhanced Activity. *Industrial & Engineering Chemistry Research* **64**, 22939-22948 (2025).

2:00pm **AA1-TuA-3 Preparing Well-defined CO_2-Conversion Catalysts using Atomic Layer Deposition**, ***Doga Özerk***, *Evgeny Pidko, J. Ruud van Ommen,* TU Delft, Netherlands

CO_2 hydrogenation to methanol is attractive, as methanol serves both as a base chemical and an energy carrier. However, due to the thermodynamic stability and low reactivity of CO_2, its conversion remains highly challenging and requires the use of efficient catalysts. Conventional catalyst synthesis methods, such as wet chemistry, often lack control over the structural and morphological properties of the materials, typically yielding catalysts with broad particle size distributions and mixed compositions. In contrast, ALD provides atomic-level precision in catalyst design, enabling the synthesis of catalysts with well-defined compositions, controlled particle sizes, and tailored active sites. This work focuses on the development of Cu and Pd-based catalysts via ALD for CO_2hydrogenation. Copper-based catalysts have been widely studied for this reaction due to their excellent hydrogen dissociation capability and cost-effectiveness compared to noble metals. However, Cu-based catalysts often suffer from nanoparticle sintering under reaction conditions, leading to catalyst deactivation through the loss of active sites and disruption of the synergistic interactions between Cu and other components in the catalyst. Pd-based catalysts have been traditionally used as Reverse Water Gas Shift catalysts, however their full potential for methanol synthesis remains underexplored. Recent studies report high methanol selectivities, yet no comprehensive mechanistic investigation has revealed the origin of this performance or established clear structure-activity relationships, due to inadequate control over Pd dispersion in conventional synthesis methods. The goal of this study is to achieve precise control over Cu and Pd dispersion and particle size at the atomic level to enhance activity and selectivity.

Cu and Pd-ALD catalysts are synthesized using $Cu(hfac)_2$ + H_2O and $Pd(hfac)_2$ + CH_2O as precursors in an atmospheric-pressure fluidized bed ALD system operating at 250 °C, with N_2 as the carrier gas. Pulse and purge times, as well as the number of ALD cycles, are varied to tune the catalyst properties. TiO_2, Al_2O_3, and CeO_2 nanoparticles (particle size: ~25 nm) are used as supports.

We will report the Cu and Pd particle size distributions on various metal oxide supports and their correlations with ALD parameters. The effect of particle size on catalytic activity and selectivity for methanol synthesis will be evaluated. The ALD-prepared catalysts will be compared to counterparts synthesized via wet impregnation. Differences in morphology, particle size, surface area and crystallinity will be discussed to elucidate structure-performance relationships.

2:15pm **AA1-TuA-4 Palladium Nanostructures by ALD for Electrocatalysis: From Single Atoms to Nanoparticles**, *Raul Zazpe, Jhonatan Rodriguez-Pereira,* ***Jan Macak***, Uni Pardubice, Czechia

This presentation is focused on the ALD growth of Pd nanostructures – from single atoms, through atomic clusters up to nanoparticles – that are deposited on various substrates and demonstrate an excellent electrocatalytic performance [1-3] for the hydrogen evolution reaction (HER).

In fact, Platinum group metals such as Pt, Ru, Pd, Ir, etc., have superior performance for various catalytic applications [4]. Due to their scarcity, efforts were being made to reduce or replace these noble metals. Atomic Layer Deposition (ALD) is one among the best technique to facilitate lowering of loading mass on a support of interest [5-7].

Due to the governing surface energy variations between noble metals and support surfaces, the growth initiates as single atoms, continues through

atomic clusters to nanoparticles (NP) and with a further increase in ALD cycles the agglomeration among NP's dominates over the individual NP size increase, thus developing thin films of relatively higher thickness.

For electrocatalytic applications, it is important to choose the right substrates. Among the available ones, carbon papers (CP) and titania nanotube (TNT) layers are best choices considering their physio-chemical properties, availability, vast literature, and low costs incurred using these as support substrates in electrocatalysis and photocatalysis.

The presentation will introduce and describe the synthesis of Palladium nanostructures – starting from single atoms, through NPs to solid films by ALD on CP substrates [1] and TNT layers with high aspect ratios [2] and QCM crystals [3]. It will also includethe corresponding physical and electrochemical characterization and encouraging results obtained in electrocatalysis.

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2:30pm **AA1-TuA-5 Controlling the Wettability and Durability of PEM Electrolysers with Plasma-Enhanced ALD of Niobium Nitride***, **Athina Tzavara-Roussi**, Volkert van Steijn, Ruud van Ommen,* Delft University of Technology, Netherlands

Green hydrogen has emerged as an effective energy storage medium, capable of buffering excess electricity generated from intermittent renewable sources. Proton exchange membrane (PEM) water electrolysers is a key technology for green hydrogen production as they offer higher efficiency, compact design and rapid response to fluctuating energy input. However, their large-scale deployment requires reducing reliance on critical raw materials while maintaining their durability.

The porous transport layer (PTL) plays a crucial role on the anodic side of PEM electrolysers. This titanium-based layer is responsible for the transport of water to the catalytic sites and the discharge of oxygen gas to the flow plates, as well as providing an electrically conductive pathway for electrons. However, the PTL faces two critical challenges that impact the performance and cost. The first challenge is the progressive growth of an oxide layer on the surface of titanium, which significantly reduces its electrical conductivity. Commercially the platinization of the titanium substrate is commonly applied to mitigate this issue, but further increases the manufacturing costs. The second challenge lies in the counter-current transport of liquid water and oxygen as dissolved gas and bubbles. This leads to the accumulation of oxygen gas within the pores of the PTL, which increases mass transport losses. This limitation becomes more pronounced at higher current densities due to higher gas production, which is otherwise advantageous for lowering the unit cost of hydrogen production.

In this work, we demonstrate the plasma-enhanced atomic layer deposition (PE-ALD) of niobium nitrides to fabricate a functional coating on the PTL surface. Niobium is an attractive candidate to replace noble metals and as nitride it can promote electron transfer to reduce ohmic losses by protecting the titanium substrate from oxidation and simultaneously being highly conductive itself. The niobium nitride coating additionally provides hydrophilicity to facilitate the water imbibition throughout the PTL, while accelerating the removal of oxygen bubbles to decrease mass transport losses. We investigate how the elemental composition, the morphology and the thickness of the niobium nitride coating influence its conductivity and hydrophilicity. Ultimately, the impact of the PTL coating on the performance and stability of a 4cm^2 PEM cell is evaluated.

This project receives a Dutch National Growth Fund contribution from the programme NXTGEN HIGHTECH.

2:45pm **AA1-TuA-6 ALD Imparts Efficiency Improvements in Proton Exchange Membrane Water Electrolyzers***, **Arrelaine Dameron**, Sara Harris, Dane Lindblad,* Forge Nano*; Alexandra Oliveira,* Mott Corporation*; JingJing Jin, Lucas Cohen, Zhexi Lin,* Columbia University*; Alexander Papandrew,* Mott Corporation*; Daniel Esposito,* Columbia University*; Matthew Weimer,* Forge Nano

Green hydrogen (H_2) offers a pathway to decarbonizing ammonia, methanol, and other chemical manufacturing processes, but widespread adoption requires achieving cost parity with hydrogen produced via steam methane reforming. Improving the electrical efficiency and achievable current density of proton–exchange membrane water electrolyzers (PEMWEs) is therefore essential for lowering the cost of green hydrogen. In this work, we use atomic layer deposition (ALD) to engineer two critical PEMWE stack components, enabling high–current–density operation at elevated cell potentials to directly enhance system efficiency and reduce cost.

A major limitation to high–efficiency PEMWE operation is the significant ohmic loss across the Nafion membrane, which becomes dominant at current densities above ~2 A cm^{-2}. Nafion is also a per– and polyfluoroalkyl substance (PFAS), raising environmental and regulatory concerns. To address these challenges, we developed zero–gap electrolyzers that employ PFAS–free, proton–conducting silicon oxide membranes fabricated via ALD. Although pristine SiO_2 exhibits proton conductivity 2–3 orders of magnitude lower than Nafion, phosphorus doping substantially enhances H^+ transport. As a result, thin (<50 nm) PO_x–doped SiO_2 membranes achieve area–specific resistances more than 10× lower than Nafion–117, while their dense structure simultaneously suppresses hydrogen crossover to acceptable levels at pressures up to ~100 bar.

A second barrier to efficient operation is the corrosion and passivation of titanium porous transport layers (PTLs) under high–potential, acidic conditions. This degradation increases interfacial contact resistance and drives voltage decay. Conventional mitigation relies on micrometer–thick noble–metal coatings (Au, Ir, Pt) applied by electrodeposition or PVD, which significantly increases system cost. Here, we investigate ultrathin ALD–deposited iridium coatings (10–20 nm) on titanium sinter PTLs. These ALD Ir coatings exhibit lower interfacial contact resistance than comparable Pt layers due to their high conductivity in both metallic and oxide states. When implemented in PEMWE cells, they support stable operation at 3 A cm^{-2} and <1.9 V for 1000 hours with no detectable voltage degradation.

3:00pm **AA1-TuA-7 Atomic Layer Deposition of Tantalum Oxide for enhanced stability of CNTs during Photoelectrochemical Water Splitting***, **Muhammad Awais Khan**,* Luxembourg Institute of Science and Technology (LIST), Luxembourg*; Diego Martinez Martinez,* luxembourg Institute of Science and Technology (LIST), Luxembourg*; Amr Nada, Nicolas Boscher,* Luxembourg Institute of Science and Technology (LIST), Luxembourg

To mitigate climate change, the global energy landscape is shifting towards hydrogen, with demand reaching 100 Mt in 2024 [1]. Photoelectrochemical (PEC) water splitting has emerged as a vital pathway for sustainable green H2 production. However, widespread implementation is hindered by thermodynamic bandgap mismatches, sluggish kinetics, and stability issues of the photo-electrocatalyst. Carbon nanotubes (CNTs) provide an ideal conductive scaffold due to their exceptional axial charge transport and high effective surface area. Despite these advantages, it has been observed that the high curvature of the graphene lattice renders CNTs susceptible to structural degradation in oxidative PEC environments [3]. Fig In particular, bare CNT electrodes exhibit severe structural degradation after 1 h chronoamperometry (CA) stability testing under illumination in 1 M KOH, as illustrated in Fig. 1. To preserve the structural integrity of CNTs, we used Atomic Layer Deposition (ALD) to deposit a protective Tantalum Oxide (Ta2O5) shell on CNTs (see Fig 2). ALD was chosen considering its sub-nanometric precision, which allows the deposition of conformal, pinhole-free films on high aspect ratio CNTs packed in a complicated forest, and the restricted carrier diffusion length in tantalum-based compounds (~50-100 nm), which demands a controlled thickness (Fig. 1). The ALD deposition process was carried out utilizing pentakis-(dimethyl-amino)-tantalum (PDMAT) and H2O as co-reactant, yielding an optimized growth per cycle (GPC) of 0.5 Å/cycle, as monitored by in-situ spectroscopy ellipsometry. X-ray diffraction (XRD) and X-ray reflectometry (XRR) confirmed the growth of dense (~6.4 g/cm3), high-purity Ta2O5 amorphous films, while X-ray photoelectron spectroscopy (XPS) verified a Ta/O ratio of 2.8 with negligible carbon contamination. Transmission Electron Microscopy (TEM) and Energy Dispersive Spectroscopy (EDS) mapping demonstrated ultra-conformal coating of Ta2O5 along the entire CNT length, ensuring complete surface passivation (cf. Fig 2). PEC performance was evaluated using cyclic voltammetry (CV), linear sweep voltammetry (LSV), electrochemical impedance spectroscopy (EIS), and chronoamperometry (CA). The Ta2O5 film significantly reduced charge-transfer resistance and effectively suppressed the morphological collapse observed in bare CNTs during stability tests (cf. Fig 1). Moreover, CA measurements under chopped illumination revealed a distinct photo-response associated with the Ta2O5 bandgap, confirming the shell's active role in the PEC process. While Ta2O5 successfully stabilizes the conductive core, its wide bandgap limits visible-

light harvesting. Consequently, this work establishes a robust baseline for transitioning toward nitrogen-doped Tantalum Oxynitride (Ta-O-N) to optimize bandgap alignment (~2.1 eV), thereby targeting theoretical solar-to-hydrogen (STH) efficiencies of up to 15.25 % with photocurrent densities of 8.1 mA cm-2 [4].

3:15pm **AA1-TuA-8 Atomic Layer Deposited AZO on Lithium Niobate: A Scalable Platform for RF Energy Harvesting and Frequency Mixing**, ***Hamed Atashbar***, University of Central Fllorida; *Hakhamanesh Mansoorzare, Terrick McNealy-James, Parag Banerjee, Reza Abdolvand,* University of Central Florida

Radio frequency (RF) signal processing and energy harvesting are critical functionalities for emerging wireless technologies. These capabilities can be effectively realized via the acoustoelectric (AE) effect, where the interaction of propagating surface acoustic waves (SAW) and electrons in thin resistive films convert acoustic energy into a DC signal or facilitate wave mixing. While previous literature has explored these effects using graphene [1] or III-V semiconductors (e.g., InGaAs) [2], these films often suffer from manufacturing scalability challenges or limited sheet resistivity control.

This work investigates the integration of atomic layer deposited (ALD) Al-doped ZnO (AZO) films with lithium niobate (LN) SAW delay lines as a robust, scalable platform for both RF-to-DC conversion and nonlinear frequency mixing. ALD AZO of 25 nm thickness were deposited on SAW devices with 100 nm thick interdigitated lines (Fig. 1). A FIJI Gen2 System from VEECO was used for the deposition, using trimethyl aluminum and diethyl zinc as Al and Zn sources and water as an oxidant. A dopant level of 2 at% was maintained while thicknesses of 20 to 30 nm were attempted on the SAW devices.

Experimental results demonstrate a linear response with a dynamic range exceeding 30 dB. Further, the devices can handle RF input powers as high as 20 dBm, generating an open-circuit voltage of 342 mV and a short-circuit current of 3 µA, measured for a device with SAW wavelength of 8 µm (FP=4 µm, 540 MHz), while the lower conversion range is masked by DC readout noise floor (Fig. 2). The device metrics enabled by ALD AZO surpass those of standard electronic rectifiers, in general, and particularly improve the conversion efficiency by more than 5.1 times relative to graphene-based counterparts.

Beyond passive detection, the platform leverages the inherent nonlinearity of the AE interaction to enable wave mixing applications. As shown in Fig. 3, fabricated AE mixers support the generation of sum and difference SAW frequencies through multi-wave mixing. This capability allows the platform to perform signal processing tasks, such as frequency conversion, entirely within the micro-acoustic domain. Crucially, the use of ALD AZO provides a commercially viable pathway for these advanced nonlinear functions, offering a distinct advantage over non-scalable III-V or graphene alternatives. These results position the AZO-on-LN platform as a versatile solution for next-generation RF sensing, harvesting, and signal processing.

ALD Applications
Room Ybor Salons I-IV - Session AA2-TuA
ALD for Batteries and Energy Storage

Moderators: Rong Chen, Huazhong University of Science and Technology, **Neil Dasgupta**, University of Michigan

4:00pm **AA2-TuA-11 Fabricating Artificial Electrode Electrolyte Interfaces for Lithium Batteries**, *Sara Pakseresht, Princess Stephanie Llanos, Filipp Obrezkov, Ville Mikkulainen,* ***Tanja Kallio***, Aalto University, Finland **INVITED**

With the growing need to increase the energy density of lithium batteries (LIBs), numerous studies have focused on developing high-capacity electrodes capable for operation at a wide potential range. Yet, extending the potential range often compromises the cycling stability because of accelerated mechanochemical ageing of the electrode active materials. Here, various coatings are applied via ALD or MLD on lithium battery electrodes to mitigate premature capacity fade. Focus is on investigating their attributes and effect of the coatings on the performance of high voltage positive electrode materials, particularly $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ (NMC811), and lithium negative electrode. Additionally, some light is shed on the synthesis of the coatings.

Such coatings as lithium titanate, titanium terephthalate and lithium fluoride are investigated on NMC811 to understand attributes of coatings, or artificial cathode electrolyte interfaces, with different chemical and physicochemical features. Due to the complex interplay of the degradation mechanisms at the crystal structure, particle, and electrode levels, *operando* XRD and dilatometry are combined with ex-situ characterization techniques to have an in-depth understanding of the mechanism of enhancement received by these coatings. The multiscale analyses show that electrodes with coated NMC811 experience more reversible variations and the applied coating improves the cycle life by suppressing various ageing processes.

As for the negative electrodes, highly reactive metallic lithium offering high capacity and most negative lithium redox potential is considered. Electrochemical measurements complemented with o*perando* dilatometry and optical measurements enable optimizing coating thicknesses to achieve a tradeoff between mechanical and chemical durability.

The reaction mechanism during ALD is studied by in-situ near atmospheric pressure XPS. Different reaction mechanisms between the NMC811 substrate and the utilized organometallic precursors are revealed. These measurements also yield information on the active role of lithium metal during the evolution of the coating.

4:30pm **AA2-TuA-13 Beyond Conventional ALD: Investigating Standalone Chemical Vapor Transformation Precursors for Battery Cathode Functionalization**, ***Donghyeon Kang***, *Jeffrey Elam,* Argonne National Laboratory

Atomic layer deposition (ALD) is a cornerstone technique for stabilizing battery interfaces, typically involving the sequential application of a metal precursor and a co-reactant to grow protective thin films. However, the inherent reactivity of battery cathode surfaces—often covered by native impurities like lithium carbonate (Li2CO3)—presents an opportunity to bypass traditional binary cycles. This study investigates the use of standalone vapor-phase precursors as a direct functionalization strategy, eliminating the need for a secondary pulse while achieving superior interfacial control.

We explore a series of aluminum (Al), phosphorus (P), and boron (B) precursors to determine their efficacy as "transforming" agents. Unlike standard ALD growth, these precursors react directly with the surface layer, converting detrimental impurities into beneficial, lithium-conducting interphases. This process effectively "cleans" the cathode surface while simultaneously depositing a sub-nanometer protective skin in a single, self-limiting step.

The reaction mechanisms are elucidated through **in situ FTIR spectroscopy**, which provides real-time evidence of carbonate consumption and the simultaneous emergence of Al-O, P-O, or B-O vibrational modes. These surface-sensitive insights are corroborated by **XPS** depth profiling and **ab initio calculation**, confirming the transformation of the cathode-electrolyte interface (CEI). Our findings demonstrate that standalone precursor exposure is a scalable and efficient alternative to conventional ALD, offering a streamlined pathway for the surface engineering of high-capacity battery materials.

4:45pm **AA2-TuA-14 Tackling Issues of Transition Metal Oxide Cathodes Using Sulfide Coatings**, ***Xiangbo Meng***, *Kevin Velasquez Carballo, Taohedul Islam,* University of Arkansas

Transition metal oxides (e.g., layered $LiNi_xMn_yCo_zO_2$) are among the most promising cathodes for next-generation lithium-ion batteries (LIBs) and beyond, but suffer from a series of structural and interfacial issues. In addressing these issues, surface modification has been proved being facile and effective. In this regard, atomic layer deposition (ALD) has emerged and offered some unrivaled benefits in coating quality and process.[1-3] In the past years, we have been investigating various coating materials [4-7] while recently, we first discovered that sulfides are very unique as coatings materials.[8-10] They can react with oxygen released from lattices of transition metal oxide cathodes, transform into sulfates, and thereby protect electrolytes from oxidation. Furthermore, the resultant sulfates as coatings still play multiple important roles in enhancing cathode performance: (1) strengtheners to maintain mechanical integrity and reduce microcracking of cathodes; (2) robust interfaces to mitigate undesirable interfacial reactions and alleviate the formation of cathode electrolyte interphase (CEI); (3) protective layers to hinder transition metal ions from dissolution, (4) structural stabilizers to suppress unfavorable phase transformation; and (5) physical barriers to inhibit crosstalk between the cathodes and anodes and to protect anodes from degradation. As a consequence, we demonstrated that sulfides are excellent surface coatings, which could dramatically improve the performance of transition metal oxide cathodes. Thus, our studies have greatly widened the search of surface coatings and provided new solutions for next-generation LIBs and beyond.

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5:00pm **AA2-TuA-15 Atomic Layer Deposition Tuned Surface Chemistry for Advanced Lithium and Manganese Rich Cathodes***, **Jahnavi Manikantan Sudharma**, Kyobin Park, Sungjoon Kim, Subhadip Mallick, Jason Croy, Donghyeon Kang, Jeffrey Elam,* Argonne National Laboratory, USA

The growing deployment of renewable energy and the rapid expansion of artificial intelligence and machine learning infrastructures place increasingly dynamic demands on modern electrical grids, requiring the need for high-performance, renewable energy-storage technologies. While nickel (Ni)-rich layered oxides remain the state-of-the-art materials for lithium-ion battery cathodes, their reliance on costly and supply-constrained Ni and cobalt (Co), motivates the development of alternative materials. Lithium- and manganese (Mn)-rich (LMR) cathodes offer a compelling solution due to their high energy density and reversible capacities enabled by anionic redox. However, oxygen loss associated with this redox process induces severe surface and interfacial degradation, including electrolyte decomposition, transition-metal migration, and Mn dissolution, which hinder long-term cycling stability of these cathodes. Suppressing Mn dissolution at the surface is still a key challenge. Advancing surface engineering, structural tuning, and electrolyte optimization is therefore critical to unlocking the full potential of LMR cathodes for next-generation energy-storage systems. Atomic layer deposition (ALD) being a self-limiting thin film growth method characterized by the sequential exposure of chemical species, offers a promising strategy to stabilize the interfaces by depositing tailored ultrathin, uniform and conformal coating layers on the surface and thereby mitigating the surface degradation of the cathode. Surface coatings applied through atomic layer deposition (ALD) offer a highly controlled route to stabilize these interfaces; however, the fundamental mechanisms governing how different ALD chemistries interact with LMR surfaces remain poorly understood. In this presentation, I will discuss our recent study combining in situ measurements of ALD chemistries, ex situ thin film characterization, and electrochemical testing of prototype batteries. By systematically investigating ALD coating chemistries including lithium phosphate (Li_3PO_4) and lithium borate ($LiBO_x$), we elucidated how ALD surface reactions govern coating composition, structure, and protective functionality and how this functionality affects cycling performance. These insights will inform rational interface-engineering strategies, enabling the practical deployment of high-energy, cobalt-lean Mn-rich cathodes for next-generation lithium-ion batteries.

5:15pm **AA2-TuA-16 Comparing Al-phosphate ALD on $LiMn_2O_4$ and SiO_2***, **Lowie Henderick**, Christophe Detavernier, Jolien Dendooven,* Ghent University, Belgium

Although lithium ion batteries (LIB) have already significantly improved, undesirable side-reactions at the electrode-electrolyte interface hamper further performance gains. Atomic layer deposition (ALD) is a promising route to improve performance via deposition of a protective coating, where materials ranging from inert (e.g. Al_2O_3 and Al-phosphate) to more conductive coatings (e.g. TiO_2 or LiPON) are being explored. ALD processes for protective coatings are typically characterized on standard native SiO_2/Si substrates and then blindly copied to the LIB electrode material. However, in situ studies have shown that the surface reactions during initial ALD cycles on battery electrodes can differ markedly from those observed on native SiO_2/Si substrates. For instance, it was shown that Al_2O_3 deposition leads to Al doping at the electrode surface[1], altering its performance. Such effects should be more properly addressed and understood if one aims to fully optimize the LIB electrode. In this work, the deposition of Al-phosphate on a $LiMn_2O_4$ (LMO) electrode is studied with in-vacuo XPS and EDX using two different ALD processes. Both processes are well understood on SiO_2, but their initial growth on a LIB electrode has not yet been addressed. On the one hand, a plasma enhanced ALD process is used consisting of TMP plasma–O_2 plasma–TMA. For this process, a 5 times higher growth rate is observed on LMO during 30 cycles compared to SiO_2. It was found that, while there is saturating growth on SiO_2, continuous polymerisation takes place on LMO due to the reactivity of the electrode surface, forming a thick phosphate-rich layer with an equivalent thickness growing beyond 15 nm after prolonged exposure (fig. 1). This highlights a significant process difference, where CVD is observed on LMO even though ALD was expected based on the process characterization on SiO_2. On the other hand, a TMP vapour–O_2 plasma–TMA–O_2 plasma process is used for which more ALD-like (self-limiting) growth can be observed on LMO. Nevertheless, based on in-vacuo XPS, it can be seen that the peak areas of the coating are approximately 70% higher during the initial cycles on LMO compared to SiO_2 (fig.2), suggesting substrate specific growth. Next to this, the P-to-Al concentration ratio also significantly differs (fig.3), further indicating a clear substrate dependency. This work highlights the importance of proper LIB interface engineering. Only by studying the deposition directly on the relevant battery electrode material, the initial growth can be fully characterized and the interface can be engineered towards next generation LIB performance. [1] Chen,L. et al., Chem, 2418 – 2435 (2018)

5:30pm **AA2-TuA-17 Unravelling the Mechanism of Al_2O_3 Atomic Layer Deposition on Li_6PS_5Cl for All-Solid-State Batteries***, Kyobin Park, Donghyeon Kang, Taewoo Kim, Vepa Rozyyev, Anil Mane, Hacksung Kim, Francisco Vargas, Zachary Hood, Peter Zapol, Justin Connell, **Jeffrey Elam**,* Argonne National Laboratory

Sulfide superionic conductors with the argyrodite structure (e.g., Li_6PS_5Cl, LPSCl) are extremely promising for all solid-state batteries, but poor atmospheric stability and high interfacial reactivity limit their widespread adoption. Coating LPSCl powders with ultrathin, metal oxide coatings using atomic layer deposition (ALD) mitigates these problems, protecting LPSCl against atmospheric degradation[1] and reducing reactivity with Li metal, yielding more stable cycling[2]. Despite significant promise, the ALD mechanism is unknown, hampering the development of new coating chemistries.

In this study, we elucidate the mechanism for Al_2O_3 ALD on LPSCl using trimethyl aluminum (TMA) and H_2O by combining *in situ* Fourier transform infrared spectroscopy measurements and *ex situ* solid-state magic angle spinning nuclear magnetic resonance, UV Raman spectroscopy, and X-ray photoelectron spectroscopy measurements with density functional theory calculations. We determine that ALD Al_2O_3 nucleates promptly via TMA reaction with native -OH, -SH, and PS_3-OH groups to form transient C-Al-O(S) species that are rapidly hydrolyzed during the subsequent H_2O exposure. This reversible transformation maintains surface nucleophilicity and prevents sulfide decomposition. The resulting layer-by-layer growth leads to highly conformal Al_2O_3 coatings on LPSCl.

This detailed understanding of ALD surface reactions provides critical insights guiding the selection of future ALD chemistries with greater enhancement in cycling performance.

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2) Hood, Z. D.; Mane, A. U.; Sundar, A.; Tepavcevic, S.; Zapol, P.; Eze, U. D.; Adhikari, S. P.; Lee, E. J.; Sterbinsky, G. E.; Elam, J. W.; Connell, J. G., Multifunctional Coatings on Sulfide-Based Solid Electrolyte Powders with Enhanced Processability, Stability, and Performance for Solid-State Batteries. *Advanced Materials* **2023,** 35, (21), 13.

ALD Fundamentals: Growth and Characterization
Room HB Plant Ballroom - Session AF1-TuA

ALD Metrology/Characterization I

Moderators: Dennis Hausmann, Lam Research, **Ruud van Ommen**, Delft University of Technology

1:30pm **AF1-TuA-1 Low Energy Ion Scattering Surface Analysis of ALD Coated Ti-Based Porous Transport Layers***, **Philipp Brüner**, Thomas Grehl,* IONTOF GmbH, Germany*; Athina Tzavara-Roussi, Rens Kamphorst, Ruud van Ommen,* TU Delft, Netherlands **INVITED**

Porous transport layers (PTLs) play a crucial role in enabling efficient electrochemical reactions in water electrolyzers. Positioned between the electrodes and the current collectors, PTLs provide structural support, help transport reactants by allowing gas diffusion and moving water from the reaction sites, provide electrical conductivity between electrode and current collector, and aid in heat dissipation for thermal management.

Titanium-based PTLs are a common choice due to good conductivity, corrosion resistance, and mechanical strength, but long-term degradation effects occur under the harsh chemical conditions encountered in an electrolyzer cell. Protective coatings help mitigate these effects and improve PTL performance by improving the chemical stability of the PTL surface and modifying surface properties.

Atomic layer deposition (ALD) is an attractive method for applying the protective coating, as it is ideally suited to porous substrates, and its conformality and precision allows fine-tuning of the thin film properties. Here, we report on low energy ion scattering (LEIS) analyses of ALD-coated Ti-based PTLs, using various coating materials.

The extreme surface sensitivity of LEIS allows quantification of the surface coverage of the ALD film, providing crucial information about film growth and layer closure. At the same time, the film thickness is evaluated to provide insight into the ALD growth mode and growth per cycle. We discuss analytical challenges associated with the highly three-dimensional nature of the deposition substrate, which affect surface quantification and film thickness measurements.

2:00pm **AF1-TuA-3 In vacuo LEIS studies on cleaning and functionalizing substrate surfaces for ALD***, Heta-Elisa Nieminen, Johanna Majlund, Marko Vehkamäki, Mykhailo Chundak, Sakari Kettunen, Matti Putkonen, **Mikko Ritala**,* University of Helsinki, Finland

Starting surfaces play a critical role for the success of ALD processes. When loaded from air to the ALD reactor, substrate surfaces have adsorbed airborne hydrocarbon molecules. While some ALD processes may be robust little affected, some others may be blocked by the hydrocarbons or products from their reactions with precursors. For example, we showed that the $Ir(acac)_3 – O_2$ ALD process deposits Ir on fresh, *in situ* deposited Al_2O_3 but not on air exposed *ex situ* Al_2O_3. On air exposed SiO_2 the Ir was deposited, however [1].

While cleaning the surfaces before loading to the ALD reactor may decrease the amount of hydrocarbons on the surface, they may be hard to completely avoid this way. Therefore, it is important to clean the surfaces in the ALD reactor and study the cleaning processes *in situ* or *in vacuo*. In this work we have used the unique ALD cluster tool where a genuine flow type ALD reactor is connected in vacuo to low energy ion scattering (LEIS), X-ray photoelectron spectroscopy (XPS) and temperature programmed desorption (TPD). With LEIS and TPD we studied Al_2O_3 and SiO_2 surfaces (i) directly after loading (*ex situ*), (ii) after heating at 300 °C, (iii) after exposing to ozone for 500 s in the ALD reactor at 300 °C, and (iv) after exposing to atomic oxygen at room temperature. *In situ* deposited Al_2O_3 served as a reference. Upon only heating to 300 °C, the hydrocarbons stay better bonded to Al_2O_3 than to SiO_2, but both the ozone and oxygen treatment clean the surfaces to a level comparable to the *in situ* Al_2O_3. We also used time-of-flight secondary ion mass spectrometry (TOF-SIMS) option of the LEIS instrument to compare hydrogen amounts on the Al_2O_3 surfaces.

SiN_x surface was studied directly after loading and after heating at 300 °C. This surface was found to have much less hydrocarbons than the two oxide surfaces. We also studied the SiO_2 and SiN_x surfaces after treatment with dilute 0.05 % HF and benzaldehyde vapor, aiming for passivation of the surfaces for area-selective deposition.

1. H.-E. Nieminen, M. Putkonen and M. Ritala, Chem. Mater. 2025, 37, 7251

2:15pm **AF1-TuA-4 ALD Outstanding Presentation Award Finalist: Operando Studies of Nitride ALD Using Ambient Pressure XPS***, **Henrik Pedersen**,* Linköpings Universitet, Sweden*; Pamburayi Mpofu, Alaa Malekshahineia, Peggy Bagherzadeh Tabrizi,* Linköping University, Sweden*; Esko Kokkonen,* Max IV Laboratory, Sweden*; Joachim Schnadt,* Lund University, Sweden

Studies of the surface chemistry of the first few cycles of ALD using *in situ* and time-resolved *operando* techniques are attractive for realizing, understanding and obtaining mechanistic information during the deposition. We will present surface-chemistry investigations through time-resolved ambient pressure X-ray photoelectron spectroscopy (APXPS) using a dedicated ALD cell[1] at the MAX IV Laboratory to study of the initial growth of TiN, AlN and GaN. While this setup has been used for oxides[2,3] and metals[4], we can here show the first results on nitrides using TDMAT, TMA and TMG/TEG with NH_3 in thermal ALD processes.

Operando APXPS is conducted concurrently with the dosing of the precursor, *i.e.*, monitoring the chemical environment of the substrate and film surface while pulsing the ALD precursors.[5] As opposed to the more common *in situ* XPS experiments that are performed after ALD half-cycles and at times under non-realistic conditions (*e.g.*, high vacuum), *operando* APXPS closely mimics or replicates actual processing environments, such as atmospheric or near-pressurized conditions.

Deposition of nitrides is a thermodynamical uphill battle as metals have a stronger driving force to form and oxide than a nitride. This is reflected in our results as an initial formation of the metal oxide, followed by slow nitridation by the ammonia. We speculate that the native oxide on silicon is acting as a source of oxygen for the initial oxidation. We also propose that this initial metal oxide formation explain long nucleation delays seen in thermal ALD of nitrides, *e.g.*, approximately 120 ALD cycles in thermal ALD of AlN.[6]

A delay in nucleation on the TDMAT-terminated surface was also observed during the NH_3 pulse. The intensity of the Ti 2p and N 1s core levels began to increase after four ALD cycles, showing that the surface was coated with Ti and N atoms and no Si signals were observed with time. The results show that ligand exchange reactions take place before transamination reactions. This was verified using the periodic changes in the intensity and peak positions of the above-mentioned spectra and complemented by residual gas analysis using mass spectrometry.

References

(1) Kokkonen et al. *Rev. Sci. Instrum.* **2022**, *93*, 013905.

(2) D'Acunto et al. *Chem. Mater.* **2023**, *35*, 529–538.

(3) Jones et al. *J. Vac. Sci. Technol. A* **2024**, *42*.

(4) Kokkonen, et al. *J. Vac. Sci. Technol. A* **2024**, *42*.

(5) Jones et al. *Surf. Sci.* **2025**, *753*.

(6) Mpofu et al. *J. Mater. Chem. C* **2024**, *12*, 12818–12824.

2:45pm **AF1-TuA-6 In-situ XPS Study of Ozone Oxidation of Aminosilane Adsorption Layers on Alumina***, **Yuki Tsuchiizu**,* Institute of Fluid Science, Tohoku university, Japan*; Daisuke Ohori,* Institute of Fluid Science, Tohoku University, Japan*; Teruhisa Ohtsuka, Masashi Yamazaki, Hiroshi Arimoto,* National Institute of Advanced Industrial Science and Technology (AIST), Japan*; Kazuhiko Endo,* Institute of Fluid Science, Tohoku university, Japan

We have determined the post-oxidation surface termination of tris(dimethylamino)silane (TDMASi) on alumina under ozone exposure using in situ XPS. Alumina was used as a reproducible hydroxylated oxide model surface for first-cycle adsorption and oxidant-half-cycle studies. A TDMASi adsorption layer on alumina was exposed to ozone for 2-20 s at 200°C. C 1s deconvolution shows that the C-N component decreases, while a high-binding-energy component at 289-290 eV increases up to 5 s. In contrast, the Al 2p-normalized N 1s signal shows no large change over 2–20 s. These results indicate that ozone cleaves C-N bonds and promotes formation of oxidized carbon species, while nitrogen-containing fragments remain on the surface. Overall, the oxidant half-cycle approaches a saturated post-oxidation surface state.

SiO_2 spacers in back-end-of-line integration require conformal deposition below 400°C with atomic-layer thickness control on 3D devices. Aminosilane precursors enable low-temperature SiO_2 ALD, and ligand variants have been developed to tune growth per cycle (GPC) and impurity behavior. This trend implies that ligand identity governs ligand-fragment incorporation during growth, so the oxidant half-cycle may yield ligand-dependent surface terminations. Because ligand-fragment retention during

early cycles can affect dielectric properties (reliability/leakage) and spacer etch response, the termination chemistry is directly relevant to BEOL SiO_2 process design. We previously used in-situ XPS to show that both the ease of initial adsorption and the adsorption structure of aminosilanes on alumina depend on ligand architecture. In this study, we use TDMASi as a case study to identify post-oxidation termination motifs under ozone.

An alumina film was deposited on a Si substrate by ALD using trimethylaluminum and O2 plasma. TDMASi was adsorbed as an initial adsorption layer, followed by exposure to ozone (≧90%) for 2-20 s at 200℃. Samples were loadlock transferred under high vacuum to in situ XPS, where Al 2p, C 1s, and N 1s spectra were acquired.

Figure 1 shows the C 1s spectra of (a) alumina, (b) before ozone exposure, and (c) after 20 s ozone exposure. The C 1s envelope was deconvoluted into C-C/C-H, C-N, C=O, and carbonate (OCOO) components. Carbonate is already present on alumina (a). Compared with (b), the C-N component decreases in (c), indicating loss of C-N bonds in amino-derived species on alumina. Figure 2 shows Al 2p normalized ozone dose time dependences of the C 1s components and N 1s. C-C/C-H, C=O, and N remain nearly constant, whereas C-N decreases and carbonate increases up to 5 s. Thus, ligand-derived N does not desorb, while ozone cleaves C-N bonds and forms carbonate species, and the reaction approaches saturation with carbonate termination.

This work was partially supported by JSPS KAKENHI 24K0786 and MEXT ARIM (JPMXP1225AT0193).

3:00pm **AF1-TuA-7 In situ and Operando investigation of MLD of Hafnicone Using Ambient Pressure-XPS**, ***Hariprasad Parayil Kalappurackal,*** Lund University, Sweden

Molecular Layer Deposition (MLD) extends Atomic Layer Deposition (ALD) by enabling the growth of hybrid organic–inorganic thin films through sequential, self-limiting surface reactions. By incorporating organic precursors into ALD-type processes, MLD (cf. Fig. 1) provides access to materials with tunable chemical functionality while maintaining the precise thickness control, conformality, and scalability of conventional ALD. Such hybrid materials are of growing interest for applications requiring tailored mechanical, electronic, or chemical properties.

Understanding MLD surface chemistry, particularly during nucleation and low-temperature growth, remains a key challenge. Here, MLD processes are studied using a dedicated ALD/MLD reactor cell integrated with ambient pressure x-ray photoelectron spectroscopy (APXPS) at the SPECIES beamline of the MAX IV Laboratory,[1A] Lund, Sweden. The setup mimics ALD reactor conditions and enables time-resolved in situ observation of surface reactions under realistic growth environments.

As a model hybrid system, we demonstrate the MLD of hafnicone[2] on silicon substrates using a deposition sequence in which the inorganic precursor TDMAHf is pulsed before the organic precursor ethylene glycol. The deposition process took place at a substrate temperature of 100℃ and the steps consists of precursor adsorption, nucleation, and saturation, which together define the deposition cycle and can be followed in real time using APXPS. As shown in Fig. 2, presence of the N 1s and Hf 4f signals from the very beginning of the measurement are due to preceding ALD experiments in the same cell: the surface is saturated by adsorbed TDMAHf already before the metal precursor pulse. Following introduction of the organic precursor, the N 1s signal completely disappears, consistent with the expected complete removal of the -NMe_2 ligands by ethylene glycol and their replacement by oxygen containing groups from the organic precursor, leading to the formation of Hf-O-C bonds characteristic of hafnicone. The shifts of the Hf 4f and C 1s core levels toward higher binding energy indicate a decrease of electron density on these atoms. The O 1s shifts towards lower binding energy. Both observations are in agreement with the formation of new oxygen bonding environments, consistent with metal organic Hf-O-C film formation. The C 1s binding energy is in line with presence of an intact ethylene linker, as expected for the present MLD process.

Hafnicone type materials are of interest due to their potential functionality, including enhanced mechanical flexibility and tunable dielectric or chemical properties resulting from the incorporation of organic linkers into a hafnium based inorganic framework.

References:

[1] Kokkonen, E. et al. Rev. Sci. Instrum. 93, 013905 (2022).

[2] Lee, B. H. et al. ACS Appl. Mater. Interfaces 6, 16880–16887 (2014).

3:15pm **AF1-TuA-8 Pyroelectric Calorimetry of MgO and ZrO_2: Untangling Thermodynamics, Kinetics, and Precursor Transport**, ***Ashley Bielinski,*** *Cong Liu, Alex Martinson,* Argonne National Laboratory

A detailed understanding of ALD surface reaction mechanisms, thermodynamics, and kinetics is essential for the development of new processes, particularly those that rely on chemical selectivity between different surface sites.While computational modeling, such as DFT can provide valuable insight on the thermodynamically favorable reactions of ALD precursor molecules, this approach is limited to simplified and idealized substrate surfaces and reaction conditions. In situ and operando studies of ALD surface reactions provide necessary information on how ALD reactions proceed on realistic substrates and under typical deposition conditions. ALD pyroelectric calorimetry provides quantitative measurements of reaction heat generation and heat transfer from surface reactions as well as precursor and byproduct flow with sufficient time resolution to measure the dynamics of these processes.

We have investigated ALD processes including the reaction between tetrakis(dimethylamido)zirconium(IV) (TDMAZr) and water to form ZrO_2 and the reaction between bis(ethylcyclopentadienyl)magnesium ($Mg(CpEt)_2$) and H_2O to form MgO using pyroelectric calorimetry.These experimental results show how practical processes both agree with and contrast computationally proposed reaction mechanisms.Additionally, we present the design of an ALD reactor customized for pyroelectric calorimetry measurements with improved timing across and array of calorimeters. Combined with reactor-scale modeling, this enhanced experimental platform gives new insight into the interplay between precursor delivery, reaction kinetics, and the role of reaction byproducts.

ALD Fundamentals: Growth and Characterization
Room HB Plant Ballroom - Session AF2-TuA
ALD Metrology/Characterization II

Moderators: Henrik Pedersen, Linköping University, Sweden, **Angel Yanguas-Gil**, Argonne National Lab

4:00pm **AF2-TuA-11 ALD Outstanding Presentation Award Finalist: Where Does the Reaction Happen? Concurrently Monitoring Ultrafast Surface and Gas-Phase Dynamics in Solid–Gas Interfacial Reactions**, *Keith Blackman, Eric Segrest, Aakash Gupta, S. Novia Berriel, Parag Banerjee,* ***Mihai E. Vaida,*** University of Central Florida

Understanding and controlling surface-limited reactions while minimizing parasitic gas-phase chemistry remains a central challenge in atomic layer deposition (ALD). Conventional in situ ALD diagnostics typically infer surface and gas-phase processes indirectly, making it difficult to disentangle their contributions. To address this, we present an experimental technique that directly distinguishes reaction products originating from the surface and the near-surface gas phase while simultaneously resolving their ultrafast dynamics, enabling detailed mechanistic insight into the underlying chemical processes. This method allows simultaneous, real-time monitoring of ultrafast reaction dynamics at the surface and above the surface during photoinduced heterogeneous reactions.

The technique combines femtosecond pump-probe spectroscopy with mass spectrometric detection, allowing concurrent observation of reaction intermediates and products formed at the solid-gas interface and within the adjacent gas phase. As a model system, we investigate the photoinduced reaction of methyl iodide on a cerium oxide surface. Species detected simultaneously from the surface and gas phase exhibit distinct signatures in the mass spectra, characterized by a sharp peak followed by a broader shoulder. Time-resolved analysis assigns the sharp peak to species emitted directly from the surface, while the broader shoulder originates from species formed in the gas phase above the surface.

By tracking the evolution of these spectral features as a function of pump-probe delay, we resolve the ultrafast dynamics governing surface-confined reactions and gas-phase processes on femtosecond to picosecond timescales. SimION simulations further corroborate the spatial origins of the detected ions. This approach enables real-time differentiation of surface and gas-phase reaction pathways, opening new possibilities for investigating precursor activation, reaction selectivity, and parasitic chemistry relevant to ALD and related thin-film deposition processes.

4:30pm **AF2-TuA-13 Dual-Box Model for In-Situ Spectroscopic Ellipsometry Data Analysis in Plasma Enhanced ALD Growth Processes**, *Ufuk Kilic, Yousra Traouli, Mathias Schubert,* ***Eva Schubert,*** University of Nebraska - Lincoln

We employ in-situ spectroscopic ellipsometry (SE) to investigate the growth dynamics of ultrathin transition metal oxide films (ZnO, WO_3, TiO_2, Ga_2O_3) during plasma-enhanced atomic layer deposition (PE-ALD). To analyze the dynamic optical response, we introduce a dual-box regression model: the first box represents surface roughness using an effective medium approximation (EMA), while the second box captures cyclic variations in the subsurface layer thickness arising from molecular rearrangements during each ALD cycle. This approach provides a time-resolved, quantitative view of both surface roughness and subsurface film growth dynamics, enabling accurate characterization of layer-by-layer deposition.

The accurate extraction of film thickness, density, and roughness at elevated substrate temperatures requires knowledge of the temperature-dependent dielectric function (TDF) of the transition metal oxides, which can significantly vary from room-temperature values. In this work, the TDF was determined via a multi-sample analysis, using optical data from films of varying thickness measured at different stages during the growth process. The incorporation of experimentally verified dielectric functions ensures that the dual-box model reliably describes the evolving optical response during high-temperature deposition, enabling detailed monitoring of sub-monolayer coverage, interface formation, and roughness evolution throughout the ALD process.

The ALD processes employ organometallic precursors with remote oxygen plasma and water co-reactants, providing controlled stoichiometry, high uniformity, and optimized interface quality. Temperature-dependent studies further elucidate the influence of surface kinetics on nucleation, growth rate, and steady-state dynamics, linking chemical reactions and surface rearrangements.

Post-deposition structural and chemical characterization, including scanning electron microscopy (SEM), atomic force microscopy (AFM), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS), corroborates the in-situ optical measurements and provides complementary insight into film crystallinity, morphology, and composition.

[1]U. Kilic, A. Mock, D. Sekora, S. Gilbert, S. Valloppilly, G. Melendez, N. Ianno, M. Langell, E. Schubert, M. Schubert, Precursor-surface interactions revealed during plasma-enhanced atomic layer deposition of metal oxide thin films by in-situ spectroscopic ellipsometry [https://scholar.google.com/citations?view_op=view_citation&hl=en&user=pAVudUUAAAAJ&cstart=20&pagesize=80&citation_for_view=pAVudUUAAAAJ:vV6vV6tmYwMC], Scientific reports 10 (1) 10392 (2020).

[2]Y. Traouli, U. Kilic, S. G Kilic, M. Hilfiker, D. Schmidt, S. Schoeche, E. Schubert, M. Schubert, In-cycle evolution of thickness and roughness parameters during oxygen plasma enhanced ZnO atomic layer deposition using in situ spectroscopic ellipsometry [https://pubs.aip.org/avs/jva/article/42/5/052403/3311662], J. Vac. Sci & Technol. A 42 (5) (2024).

4:45pm **AF2-TuA-14 Imaging Ellipsometry with LHAR Test Structure for Characterizing ALD Conformality**, ***Hiroshi Nishizato,*** Kumamoto University, Japan*; Yugo Nakaya,* HORIBA STEC, Co., Ltd., Japan*; Lianhua Jin,* University of Yamanashi, Japan*; Takeshi Momose,* Kumamoto University, Japan

We developed a novel methodology to quantitatively evaluate the penetration depth (PD) of films in three-dimensional (3D) features deposited by atomic layer deposition (ALD), combining our developed imaging ellipsometry with an in-house lateral high-aspect-ratio (LHAR) test structure. The effectiveness of this methodology was confirmed using ALD Al_2O_3 from trimethylaluminum (TMA) and H_2O.

ALD is widely used in the fabrication of 3D semiconductor devices that require high conformality. The PD is a consequence of ALD kinetics, including adsorption, desorption, and surface reactions; therefore, it is a critical parameter for assessing conformality in such complex 3D architecture. PD was thus evaluated using the LHAR structure comprising a Si substrate with a shallow, wide groove at the edge, capped with a quartz plate. The LHAR structure has an aperture of 20 μm × 4 mm and a depth of 6 mm. Sample imaging was enabled by installing an Offner optical system on our custom-built ellipsometer, allowing the PD formed in a groove on the Si substrate to be determined. To enhance imaging contrast, the retarders were set to 150° on the light-source side and 30° on the camera side, while both polarizers were set to 0°. The ALD Al_2O_3 film, with a thickness of 6-60 nm, was captured under these settings. Experimental results showed that the growth per cycle (GPC) measured on planar Si substrates with a 3 nm thermal SiO_2 underlayer was independent of the TMA dosing, while the PD in the LHAR structure increased with increasing TMA dosing. In this manner, we established a methodology to evaluate PD using imaging ellipsometry with the LHAR test structures. As it is in an offline setting, we plan to install them in an ALD chamber for real-time PD monitoring. On such occasions, precise control of the concentration and supply duration of both the precursor and the reactant is essential for accurately determining time-dependent PD evolution. Therefore, a piezoelectrically controlled vapor delivery system has already been installed on our ALD equipment for both TMA and H_2O, enabling precise, rapid dose control by adjusting the valve opening ratio and duration.

References

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5:00pm **AF2-TuA-15 Surface Chemistry Investigation for ALD of SiOCH Using in-Situ Reflection Absorption Infrared Spectroscopy (RAIRS)**, ***Sjoerd van der Werf,*** Eindhoven University of Technology, Netherlands

There is a need to replace silicon nitride inner spacers in gate-all-around field-effect transistors by low-k materials to reduce parasitic capacitance in these 3D architectures. Atomic layer deposition (ALD) is the method of choice for the fabrication of this material, due to the need for good conformality for this application. For this work the specific interest is in the surface chemistry that occurs throughout potential half-cycles to establish successful ALD cycles for carbon-containing SiO2.

The study focused on the adsorption of the silicon-carbon precursor BTDMASM (composed of two silicon atoms bridged by a CH2 group and six ligands), by identifying relevant surface groups and looking into the reaction of the surface groups with different reactants. These reactants include water, ethylene glycol, and an organic acid. In addition, more complex chemistries were considered, including ABC-type approaches, for example to activate surface groups or more efficient ligand removal.

The surface reactions were studied using in-situ RAIRS measurements, which resulted in a clear understanding of the surface reactions during an ALD cycle. For example, the organic acid was shown to react with the ligands of BTDMASM very efficiently, where all ligands are removed upon exposure to the acid. The adsorption of the organic acid on the surface leads to the removal of surface attached ligands from the precursor, which is observed in the CH stretch region as well as based on C=O and C-O bonds.

The data on the adsorption of BTDMASM on SiO2 suggests that the precursor is susceptible for adsorbing on hydroxyl groups. The organic acid does not result in the replenishment of reactive adsorption sites. Therefore, water was introduced as a second co-reactant to remove the acid and replenish hydroxyl groups, which is observed by the removal of groups related to the adsorbed acid. The removal of the organic acid is temperature dependent where for a temperature of 350 C degrees the C=O and C-O bonds are no longer present at the surface. The surface chemistry of water and the acid in combination with BTDMASM was investigated for different conditions, where temperature series have shown that the surface groups are temperature dependent, as is subsequent precursor adsorption. Overall, a better understanding is achieved regarding the surface chemistry for the thermal ALD of SiOCH with the use of RAIRS.

Atomic Layer Etching

Room Tampa Bay Salons 3-4 - Session ALE1-TuA

Plasma and Energy-enhanced ALE II

Moderators: Harm C.M. Knoops, Oxford Instruments Plasma Technology, Netherlands, **Nicolas Possémé**, CEA-Leti

1:30pm **ALE1-TuA-1 Etch Characteristics of Iridium with Atomic Layer Etching Technique**, ***Wendy Yan,*** IBM Research **INVITED**

Iridium (Ir) is a promising replacement for copper (Cu) in next-generation interconnects, yet its plasma etching is limited by low-volatility reaction products. This work investigates Ir plasma atomic layer etching (ALE) using Cl/O_2 and CF_4/O_2 chemistries. The ALE sequence employs oxygen-assisted halogenation for surface modification, followed by low-energy ion activation to enable directional desorption of Ir-containing byproducts.

Etching mechanisms are examined using X-ray photoelectron spectroscopy (XPS), time-of-flight secondary ion mass spectrometry (TOF-SIMS), and transmission electron microscopy (TEM). XPS identifies Ir–Cl, Ir–F, and Ir–O bonding states, TOF-SIMS quantifies modified layer thickness and molecular distribution, and TEM probes small critical-dimension feature profiles and sidewall chemical composition. Correlating these surface and structural analyses with etch-per-cycle, profile anisotropy, line-edge roughness, and hardmask selectivity enables a better understanding of Ir ALE characteristics and guides the optimization of Ir interconnect pattern fidelity and dimensional control.

2:00pm **ALE1-TuA-3 Selectivity, Surface Roughness and Residue of Plasma-Based Atomic Layer Etching of Metals and Dielectric Materials for Semiconductor Devices***, **Heeyeop CHAE,*** Sungkyunkwan University (SKKU), Republic of Korea

The critical dimensions of semiconductor devices continue to shrink, reaching nanometer and even angstrom scales in both 2D and 3D structures. Consequently, the demand for atomic-scale precision in etching processes is rapidly increasing. This talk will present various examples of plasma-based atomic layer etching (ALE) with emphasis on etch selectivity, surface roughness, and residue control for both metal and dielectric materials. Materials discussed include silicon nitride, titanium nitride, zirconium oxide, silicon oxide, aluminum oxide, hafnium oxide, molybdenum, ruthenium, and tantalum nitride. Typical ALE processes consist of two sequential steps: surface modification and material removal. Surface modification is achieved through various reaction pathways, including fluorocarbon film deposition, surface fluorination, chlorination, and oxidation using plasma-generated radicals. In the subsequent removal step, the modified layers are eliminated through mechanisms such as ion bombardment, thermal desorption, ligand exchange, ligand volatilization, or halogenation. This talk will also address key characteristics of plasma-based ALE processes, including etching selectivity, surface roughness, and residual surface contamination.

2:15pm **ALE1-TuA-4 Directional Atomic Layer Etching of MgO-Doped Lithium Niobate Using Br-Based Plasma***, **Ivy Chen,*** California Institute of Technology*; Frank Greer,* Jet Propulsion Laboratory (NASA/JPL)*; Austin Minnich,* California Institute of Technology

Lithium niobate ($LiNbO_3$, LN) is a nonlinear optical material of high interest for integrated photonics with applications ranging from optical communications to quantum information processing. The performance of on-chip devices based on thin-film lithium niobate (TFLN) is presently limited by fabrication imperfections such as sidewall surface roughness and geometry inhomogeneities over the chip. Atomic layer etching (ALE) could potentially be used to overcome these difficulties. Although an isotropic ALE process for LN has been reported, performing LN fabrication completely with ALE faces several challenges, including the lack of a directional ALE process for pattern transfer and the redeposition of involatile compounds. We report a directional ALE process for LN consisting of sequential exposures of HBr/BCl_3/Ar plasma for surface modification and Ar plasma for removal. The HBr chemistry is found to decrease redeposition compared to F- and Cl-based plasmas, which we attribute to the higher vapor pressures of Br-based products. A grating pattern etched entirely by the process (total etch depth of 220 nm) exhibits no aspect ratio dependent etching (ARDE) down to the smallest tested gap of 150 nm, in contrast to ion milling in which ARDE manifests even at 300 nm gaps for the same etch depth. The HBr plasma chemistry is also found to support an isotropic process consisting of sequential exposures of H_2 plasma and HBr/BCl_3/Ar plasma. These processes could be used together to perform the complete fabrication process for TFLN devices, eliminating imperfections arising from ion milling.

2:30pm **ALE1-TuA-5 Examining AlGaN Atomic Layer Etch per Cycle Uniformity and Repeatability by Cross-Referencing In-Situ Etch Depth Monitoring with Electrical Characterisation***, **Ben Jones,*** *Matthew Loveday, Sung-Jin Cho, Andrew Newton,* Oxford Instruments Plasma Technology, UK

Atomic layer etching (ALE) of AlGaN is well suited to the critical gate recess step of AlGaN/GaN normally-off metal insulator semiconductor-high electron mobility transistors (MIS-HEMT) [1]. A two-dimensional electron gas (2DEG) forms at the AlGaN–GaN interface (**Fig. 1**) enabling the mobility and carrier density required for high–performance power devices. As shown in **Fig. 2**, 2DEG mobility directly governs device efficiency [2]. Its formation depends strongly on AlGaN film properties and thickness. Precise control of the AlGaN gate–recess thickness is essential for engineering threshold voltage (V_{TH}) and blocking capability, ideally ~5 nm thickness [3]. Low–damage processing is necessary to minimise interface traps, leakage, and electric–field crowding [4].

Using a reflectance-based endpoint technique, sub-5 nm AlGaN films have been etched with Cl_2/BCl_3 ALE. **Fig. 3** plots dose time vs etch–per–cycle (EPC) for 30 - 120 ms doses, with a clear EPC jump at 40 ms and plateauing thereafter, indicating saturation. Process repeatability is demonstrated in **Fig. 4**: across 11 runs, EPC ranged from 0.79–0.88 nm/cycle. The normal distribution of this data set is plotted in **Fig. 5**, indicating run-to-run EPC uniformity of 5.4 %. However, reflectance end pointing only measures the targeted point and gives no cross–wafer EPC uniformity. Such uniformity is difficult to measure on <10 nm AlGaN due to surface roughness, ellipsometry limits, and FIB/SEM damage. We aim to infer etched film uniformity by correlating reflectance–measured AlGaN thickness with sheet resistance obtained via Hg–probe analysis. **Fig. 6** shows in–situ thickness measurements for targeted 5 nm and 0 nm endpoints, illustrating the strength of the technique: the ALE sequence stops automatically when the desired thickness is reached [5]. **Fig. 7** displays raw reflectance data; the initial smooth region occurs before the “turning point,” after which true thickness is extracted, shown by the stepped profile. Accurate end thickness does not require knowledge of the initial AlGaN thickness.

In this submission we will quantify EPC uniformity across Ø150 mm AlGaN–GaN substrates by combining in–situ reflectance thickness measurement with local Hg–probe C–V/I–V sheet–resistance mapping. We will also electrically characterise surface roughness of sub–5 nm AlGaN films produced by ALE and ICP etching. Finally, we will expand the current dataset to show how etch–process parameters influence run–to–run uniformity across multiple AlGaN–GaN wafers.

2:45pm **ALE1-TuA-6 Atomic Layer Etching Techniques for Sidewall Surface Damage Removal in GaN-Based LEDs***, Chan Ho Kim, Sung Hyun Kim, Young Woo Jeon, Jong Woo Hong, Jong Soon Park,* ***Geun Young Yeom,*** Sungkyunkwan University, Republic of Korea **INVITED**

As the GaN light emitting diode (LED) device technology is developed from conventional LED to micro LED, the lateral dimension of LED devices is decreased, and the ratio of sidewall area relative to overall device area is increased. Especially, as the GaN LED device size decreases below 5 microns, the performance and reliability of GaN devices are significantly degraded. One of the reasons for the degradation of the micro LED device is the damage from the sidewall due to the ion bombardment during the reactive ion etching (RIE).Ion bombardment during the RIE can lead to various issues such as surface composition changes, surface defects, surface contamination, and increased leakage current.

In this study, we focused on the etching of GaN LED devices with a multi quantum well (MQW) layer, which is composed of multiple InGaN and GaN layers. A mesa structure of GaN LED device consisted of p-GaN/MQW/n-GaN/undoped-GaN layer on sapphire wafers (or silicon wafers) was etched using BCl_3/Cl_2/Ar RIE, and the sidewall damage remaining after the RIE was removed using wet etching and/or ALE methods using conventional ICP etch system and an ion beam-based etch system. The effect of wet etching of damaged GaN LED sidewall using a KOH-based solution was compared with the sidewall damage removal using ALE methods. The effect of ion beam-based ALE on the removal of sidewall damage for vertical GaN LED devices will be also discussed. The results showed that, the wet etching improved the sidewall stress or defects due to the damage by RIE, however, the optimized ALE processes removed the sidewall stress and defects on MQW layers of patterned GaN structure almost completely. This indicates that, as GaN-based devices decrease in size, the effectiveness of ALE increases, making ALE more effective than wet etching for removing sidewall etch damage for next-generation device fabrication.

Atomic Layer Etching
Room Tampa Bay Salons 3-4 - Session ALE2-TuA
ALD+ALE and Selective ALE

Moderators: Jean-François de Marneffe, IMEC, **Austin Minnich**, Caltech

4:00pm **ALE2-TuA-11 Self-Limiting Oxidation State Control of MoOx Thin Films Using Integrated ALD and ALE***, **Woojin Jeon,*** *Chaeyeong Hwang,* Kyung Hee University, Republic of Korea*; Christophe Vallée,* University at Albany-SUNY **INVITED**

Atomic layer etching (ALE)has evolved beyond its intrinsic advantage of precise thickness controllability, and low-damage etching, with increasing research focused onadvanced process applicationssuch as the crystallization of ultrathin films as well as the realization ofgate-all-around

(GAA)andthree-dimensional (3D) integrationstructures through integration withatomic layer deposition (ALD)andarea selective deposition (ASD).

In this talk, we present our research results oncontrolling the oxidation state of deposited thin films through the integration of ALD and ALE processes. Molybdenum dioxide (MoO_2) has attracted significant attention as a high-work-function electrode material for next-generation metal-insulator-metal (MIM) capacitors, particularly for stabilizing the rutile phase of TiO_2 with a dielectric constant of 150. However, typical ALD process only allows the most stable oxidation state of MoO3, resulting in stoichiometric variations in high-aspect-ratio structures and morphology degradation during reduction have limited its practical applications. To address these issues, we introduce an approach which combines ALD of MoO_a ($2 < a < 3$) followed by ALE of MoO_3 using H_2O. The process selectively removes MoO_3through etching, leveraging the self-limiting nature of both reactions to achieve precise atomic-scale control over oxidation states without morphology degradation. MoO_2 films deposited using this method exhibit enhanced electrical performance, including a higher dielectric constant and reduced leakage current when employed as bottom electrodes in TiO_2-base MIM capacitors.

4:30pm **ALE2-TuA-13 Selective Etching of Molybdenum and Tungsten Oxides Based on Their Oxidation States Using $SOCl_2$ and SO_2Cl_2**, ***Troy Colleran,*** University of Colorado at Boulder

Molybdenum, tungsten, and their oxides have important applications in microelectronics processing. This investigation explored the spontaneous etching of MoO2, MoO3, WO2, and WO3 by thionyl chloride (SOCl2) and sulfuryl chloride (SO2Cl2). The studies were conducted at 200°C using quadrupole mass spectrometry (QMS) and in situ Auger electron spectroscopy (AES). The QMS studies revealed selectivity between the +4 and +6 oxidation states of the metal oxides using SOCl2 and SO2Cl2 as the etchants. The in situ AES experiments demonstrated the removal of native oxide on both W and Mo thin films using SOCl2.

SOCl2 etched MoO3 and WO3 in the +6 oxidation state and produced MoO2Cl2 and WO2Cl2 and WOCl4, respectively. These volatile Mo and W oxychloride etching products were verified by QMS using their isotopic signatures (Figures 1 & 2). In contrast, SOCl2 did not etch the +4 oxidation state in MoO2. However, SOCl2 did etch WO2. SO2Cl2 displayed nearly opposite behavior. SO2Cl2 etched the +4 oxidation state in MoO2, but did not etch the +6 oxidation state in MoO3. SO2Cl2 also did not etch either WO2 or WO3. The lack of etching of WO2 by SO2Cl2 and the etching of WO2 by SOCl2 was attributed to the oxidation and disproportionation of WO2 to WO3.

In situ AES studies were used to evaluate the ability of SOCl2 to remove native oxide from Mo and W surfaces. After SOCl2 exposure at 250°C, the atomic percentage of oxygen on the metal films dropped from 59% on Mo and 53% on W before SOCl2 exposure to <2% on both films after SOCl2 exposure (Figures 3 and 4). SOCl2 has the potential to remove oxides on conductive Mo and W lines in BEOL interconnects. Oxidation and subsequent volatilization of the formed oxide also is a method for the thermal atomic layer etching (ALE) of Mo and W metals.

4:45pm **ALE2-TuA-14 High-Density Silicon Lines Patterning with Atomic Layer Etch Pitch Splitting (APS™) Technology**, ***Amin Karimi,*** *Robin Athle, Reza Jafari Jam, Alfred Ahlström Andersson, Svetlana Ivanova, Kishwar Sultana, Asif Muhammad, Mostafa Torbati, Hesamedin Safavi,* AlixLabs A.B., Sweden*; Fred Roozeboom,* University of Twente, Netherlands*; Dmitry Suyatin, Jonas Sundqvist,* AlixLabs A.B., Sweden

Dense silicon line fabrication is a central process in modern electronics manufacturing, enabling key device and interconnect structures such as FinFETs, gate-all-around FETs (GAA-FETs), gate electrodes, and metal interconnects.These features appear across multiple integrated-circuit layers, from front-end devices to back-end of line metallization layers (M0–M6), and are essential for logic and memory technologies. As device scaling continues, the ability to pattern denser line arrays with tighter pitch and smaller critical dimensions (CDs) has driven innovation. To meet scaling demands, advances in lithography and patterning have included deep ultra violet (DUV) immersion lithography, nanoimprint lithography (NIL), and low- and high-NA extreme ultraviolet (EUV) lithography. In parallel, multipatterning schemes such as SADP, SAQP, LELE, and SALELE have been developed to extend resolution limits. However, each approach has limitations. Immersion lithography faces fundamental resolution constraints, NIL suffers from defectivity and throughput challenges, and EUV adoption is hindered by very high capital and infrastructure and energy costs. Multipatterning further increases process complexity through repeated deposition, lithography, cleaning, and etching steps, leading to cumulative yield loss and stricter process control chalenges. As patterns reach a 24nm pitch and below, the high-aspect-ratio mandrils used to form silicon fins and nanosheets become prone to mechanical bending or collapse during the multiple deposition and etching cycles required by SAQP.

In this work, we present Atomic Layer Etch Pitch Splitting (APS™) patterning technology developed at AlixLabs[1-4] that simplifies dense line fabrication while extending the resolution of conventional lithography. The method is based on atomic layer etching (ALE) and serves as a more sustainable alternative to conventional multipatterning. It enables significant pitch reduction with a single processing step, reducing the need for EUV at certain technology nodes. In this way, patterns defined at 14/12 nm using immersion lithography can be scaled to effective dimensions corresponding to 7/6 nm and beyond, without EUV, lowering complexity and cost. The technique operates on patterns with arbitrary topology, including straight and inclined features, enabling orientation-independent line splitting. We demonstrate silicon dense line arrays with CDs of 10 nm and half-pitch of 10 nm. The process is repeatable, allowing multiple successive splitting steps equivalent to SAQP. Our single-step patterning process alternative, APS™, reduces yield variation and eliminates intermediate metrology needs.

1. Khan Md S. A., et al. US10930515 B2, Feb. 23, 2021, priority date March 14, 2017.

2. Khan Md S. A., et al. US11424130 B2, Aug. 23, 2022.

3. Khan Md S. A., et al., US20250259851 A1, Aug. 14, 2025.

4. Sundqvist J., et al. 13429, p. 134, SPIE, Apr. 22, 2025.

5:00pm **ALE2-TuA-15 Direct Atomic Layer Processing (DALP®): Extending ALD and ALE to Spatially Localized Multi-Material Integration**, ***Mira Baraket,*** ATLANT 3D Nanosystems, Denmark

The development of next-generation electronic and functional devices increasingly depends on the ability to integrate complex material heterostructures with nanoscale precision. However, conventional thin-film deposition and patterning workflows—while offering excellent uniformity and material quality—remain inherently rigid, limiting spatial selectivity, multi-material integration, three-dimensional thickness control, and rapid experimentation within a single process flow.

ATLANT 3D introduces **Direct Atomic Layer Processing (DALP®)**, a nanofabrication technology that enables digitally controlled, spatially localized deposition of multiple materials with atomic-scale precision. DALP combines the strengths of atomic layer deposition with direct-write spatial control, allowing different materials to be sequentially deposited at defined locations without intermediate lithography or masking steps. This capability enables the fabrication of complex material stacks, heterostructures, interfaces, and thickness gradients within a unified and repeatable workflow.

This presentation describes the DALP process architecture and its application across both combinatorial materials discovery and targeted device manufacturing. By enabling programmable material placement, precise thickness engineering, and high process repeatability within a single platform, DALP accelerates materials exploration while directly producing device-ready structures compatible with manufacturing environments. Representative examples demonstrate multi-material nanoscale structures for advanced semiconductor and functional material applications, where precise interface control, spatial selectivity, and scalability are critical.

DALP significantly expands the accessible design space for atomic-scale fabrication and provides a direct pathway from materials discovery to manufacturable, device-ready architectures.

5:15pm **ALE2-TuA-16 Atomic Layer Etching of Titanium Nitride with O_3 and $NbCl_5$**, ***Juha Ojala,*** *Mykhailo Chundak, Anton Vihervaara, Mikko Ritala,* University of Helsinki, Finland

Titanium nitride is an essential material in the semiconductor industry, used as a gate metal and as electrode material in various devices, and as a diffusion barrier in metal interconnects. Future device architectures require materials to be formed into smaller and increasingly complex features, which drives the need for new deposition and etching processes. Thermal atomic layer etching, as an isotropic and conformal process is ideal for thinning and patterning films in high aspect ratio and non-line-of-sight structures. In some cases, ALE can also result in smoothing of the film surface, which could be used for interfacial engineering to improve device performance.

We present a new thermal atomic layer etching process for TiN based on oxidation of the TiN surface with O_3, and removal of the oxidized surface layer with $NbCl_5$. The process was studied at 200–350 °C and EPC values of 0.5–4.5 Å were observed. At 200–300 °C an Arrhenius type temperature dependence of the EPC was seen. Roughnesses of the films were studied using atomic force microscopy and it was found that at 200 °C the etching resulted in smoothing of the TiN surface from 0.7 to 0.6 nm RMS. The surface roughness was quite low even after etching at higher temperatures, as etching at 250–350 °C resulted in only slight roughening to about 0.9 nm RMS. Resistivities of the films were also measured, and it was found that the resistivity stayed comparable to the unetched film to a thickness of 4.5 nm. XPS measurements showed the presence of slight niobium oxide residue on the surface of partially etched TiN, but after full etching of the TiN film, no residues of the etchants could be seen.

Emerging Materials and Processes
Room Tampa Bay Salons 1-2 - Session EM1-TuA
Next Generation ALD Semiconductors

Moderators: Neeraj Nepal, U.S. Naval Research Laboratory, **Junjie Zhao**, Zhejiang University

1:30pm **EM1-TuA-1 Real-time Optimization of Gallium Oxide and Aluminum Gallium Oxide Thin Film Growth via Plasma-Enhanced Atomic Layer Deposition Using In-situ Spectroscopic Ellipsometry***, Yousra Traouli, Ufuk Kilic, Mathias Schubert, Eva Schubert,* University of Nebraska - Lincoln

Ultrawide bandgap metal oxide semiconductor materials have attracted significant interest for high-power, high-frequency, and extreme-environment applications due to their large breakdown fields and thermal stability under harsh operating conditions. In this work, we investigate the growth dynamics of gallium oxide (Ga_2O_3) and aluminum gallium oxide ($(Al_xGa_{1-x})_2O_3$ thin films deposited by plasma-enhanced atomic layer deposition (PE-ALD). The deposition process was monitored in real-time using *in-situ* spectroscopic ellipsometry (SE).

Ga_2O_3 ultrathin films were grown using four trimethylgallium pulses with a total exposure time of 20 msec during the metal-precursor half-cycle, followed by a remote oxygen plasma (75 sec, 300 W). Ternary $(Al_xGa_{1-x})_2O_3$ films were deposited using a hybrid ALD process that alternate trimethylaluminum (60 msec)/H_2O (60 msec) cycles for Al_2O_3 and trimethylgallium/oxygen-plasma cycles for Ga_2O_3. While the substrate temperature is maintained at 250 ° C, argon was used Argon as the carrier gas during the introduction of precursor material (60 sccm) and plasma process (200 sccm) with process pressure of 0.25 Torr.

To interpret the time-resolved SE data, a dynamic dual-box model approach was employed, providing insight into surface processes such as precursor adsorption and ligand removal [1,2]. Periodic oscillations in surface roughness and subsurface layer thickness were observed, reflecting the cyclic nature of molecule attachment and ligand desorption. To maintain accurate analysis of the *in-situ* SE data,the complex dielectric functions of Ga_2O_3 and $(Al_xGa_{1-x})_2O_3$ thin films were determined over the spectral range of 0.74–5.04 eV using selected *in-situ* SE data at different film thickness. The growth rates of Ga_2O_3 and Al_2O_3 were 0.918 Å/cycle and 0.575 Å/cycle, respectively. Additionally, by performing *ex-situ* SE measurements in a spectral range from 0.64 eV to 9 eV at select angles of incidence from 45° to 75° by 10° steps, we extracted the broad spectral range complex dielectric function at room temperature and identify the higher order band-to-band transitions based on critical point model dielectric function analysis.

Complementary characterization techniques, including X-ray diffraction, X-ray photoelectron spectroscopy, and atomic force microscopy, were used to assess film crystallinity, composition, and surface morphology.

Overall, this study demonstrates the *in-situ* SE technique as a powerful tool for recipe optimization and for revealing in-cycle growth kinetics during PE-ALD of Ga_2O_3 and $(Al_xGa_{1-x})_2O_3$ thin films.

[1] Kilic, Ufuk, et al. Sci. Rep. 10.1 (2020): 10392.

[2] Traouli, Yousra, et al. J. Vac. Sci. Technol. 42.5 (2024).

1:45pm **EM1-TuA-2 Conductive Si-Doped Ga_2O_3 via Thermal ALD Followed by Thermal Annealing***, Benjamin Greenberg,* U.S. Naval Research Laboratory*; Katie Gann,* National Research Council Fellow Residing at U.S. Naval Research Laboratory*; Boris Feigelson, Alan Jacobs, Jeffrey Woodward, Daniel Pennachio, Emma Rocco,* U.S. Naval Research Laboratory

Monoclinic β-Ga_2O_3 has a rare combination of ultrawide bandgap (~4.8 eV) and extrinsically controllable electron density, n, between ~10^{16} and ~10^{20} cm^{-3}, making it a strong candidate for high-power, high-frequency, and optoelectronic applications. There have been numerous reports of β-Ga_2O_3 thin film growth via metalorganic chemical vapor deposition (MOCVD), thermal atomic layer deposition (ALD), and plasma-enhanced atomic layer deposition (PEALD), including Ga_2O_3:Ge with $n > 10^{20}$ cm^{-3} via MOCVD[1] and Ga_2O_3:Si with $n > 10^{18}$ cm^{-3} via PEALD followed by thermal annealing.[2] In the case of thermal ALD, conformal growth on substrates with high aspect ratio (AR) has been demonstrated, including Si trenches with AR = 11,[3] although doping of the conformal Ga_2O_3 was not investigated. For the development of high-performance, high-AR Ga_2O_3 devices, there remains a need for thermal ALD processes for doped Ga_2O_3 that can simultaneously achieve high n and high conformality.

In this work, we demonstrate thermal ALD of Ga_2O_3:Si using trimethylgallium (TMG), bis(t-butylamino)silane (BTBAS), and ozone as precursors, employing supercycles consisting of x TMG/O_3 cycles and 1 BTBAS/O_3 cycle. Amorphous Ga_2O_3:Si is deposited on Si(100), α-Al_2O_3(0001), and insulating β-Ga_2O_3:Fe(010) substrates at 220 °C, and some films are then crystallized via thermal annealing under N_2. Comparing as-grown Ga_2O_3:Si with x = 15 to undoped Ga_2O_3, Si incorporation is confirmed by an increase in the growth-per-cycle (GPC) from 0.69 to 0.73 Å/cyc and a decrease in the refractive index from 1.92 to 1.84. The as-grown films are electrically insulating, but thermal annealing experiments reveal that low electrical resistivity is possible after crystallization. Ga_2O_3:Si (x = 400, thickness = 28 nm) grown on β-Ga_2O_3:Fe and annealed at 900 °C for 10 min exhibits $n = 8.4 \times 10^{18}$ cm^{-3} (dopant activation = 8.8%) and an electron mobility, μ, of 49 $cm^2V^{-1}s^{-1}$ for a resistivity, ρ, of 1.4×10^{-2} Ω-cm. Interestingly, ρ becomes immeasurably high (ρ > 1 Ω-cm) when the annealing temperature is increased to 1000 °C. X-ray diffraction (XRD) and transmission electron microscopy (TEM) indicate that annealing at 900 °C produces an epitaxial β-Ga_2O_3:Si layer on top of the β-Ga_2O_3:Fe that spans approximately half of the film thickness (with lower crystalline quality in the top half of the film), whereas annealing at 1000 °C produces fully epitaxial β-Ga_2O_3:Si. The high ρ of the fully epitaxial β-Ga_2O_3:Si—and potential strategies for attaining conformal, conductive β-Ga_2O_3:Si on various substrates—will be discussed in light of known challenges presented by Ga_2O_3 crystallization, including the possible formation of Ga vacancies[4] and γ-Ga_2O_3 en route to β-Ga_2O_3.[5]

1. Alema *et al.*, *APL Mater.* 9, 091102 (2021)
2. Zhang *et al.*, *Surf. Coat. Technol.* 435, 128252 (2022)
3. Comstock & Elam, *Chem. Mater.* 24, 4011 (2012)
4. Gann *et al.*, *J. Appl. Phys.* 138, 115302 (2025)
5. Wouters *et al.*, *APL Mater.* 12, 011110 (2024)

2:00pm **EM1-TuA-3 Low-Temperature Self-Limiting Growth of Crystalline III-Nitride Films: How Far Can We Go?***, Necmi Biyikli,* University of Connecticut **INVITED**

2:30pm **EM1-TuA-5 Piezoelectric and ferroelectric $Al_{1-x}Sc_xN$ by plasma-enhanced ALD***, Gilbert B. Rayner Jr., Noel O'Toole, Nathaniel Nelson,* Kurt J. Lesker Company*; Bangzhi Liu,* The Pennsylvania State University*; Jeffrey Shallenberger,* The pennsylvania State University*; Gregory Muha, Piush Behera, Suraj Cheema,* Massachusetts Institute of Technology*; Blaine Johs,* Film Sense*; Nastazia Moshirfatemi,* General Technical Services, LLC*; Daniel Drury, Brendan M. Hanrahan,* Army Research Directorate, DEVCOM Army Research Laboratory*; Glen R. Fox,* Fox Materials Consulting, LLC*; Nicholas A. Strnad,* Army Research Directorate, DEVCOM Army Research Laboratory

Wurtzite aluminum–scandium nitride ($Al_{1-x}Sc_xN$) thin films are promising for next-generation electronic and sensing technologies. However, achieving precise composition and uniform coverage on complex three–dimensional architectures remains challenging. Here, we demonstrate the growth of $Al_{1-x}Sc_xN$ by plasma–enhanced atomic layer deposition (PEALD) under ultrahigh purity conditions (UHP-C) using a supercycle sequence composed of alternating AlN and ScN constituent processes. The PEALD process utilized trimethylaluminum (TMA), bis(ethylcyclopentadienyl) scandium chloride [$ClSc(EtCp)_2$] and N_2−H_2 plasma as co-precursors at substrate temperatures ranging from 215−300 °C.

A 60.3 nm-thick PEALD $Al_{0.83}Sc_{0.17}N$ film grown at 300 °C on a {111}-oriented platinum bottom electrode on Si (100) exhibited clear ferroelectric switching. The film showed switched polarization ($2P_r$) of 163 μC/cm^2 and 139 μC/cm^2 for negative and positive pulsing, coercive fields of 5.5 MV/cm and -4.8 MV/cm, and a dielectric constant of 12.8−13.8 at 100 kHz under ±10 V. The effective longitudinal piezoelectric coefficient ($d_{33,f}$) of the $Al_{0.83}Sc_{0.17}N$ film was measured to be -23.6 pm/V and 22.1 pm/V for the N- and metal-polarities, respectively.

Structural analysis revealed that the film on {111} platinum was fully c-axis (0001) oriented out-of-plane, indicating high crystalline quality even along the sidewalls of three–dimensional features. When deposited on single–crystal gallium nitride, the $Al_{0.83}Sc_{0.17}N$ adopted a highly ordered in-plane and out-of-plane arrangement consistent with epitaxial growth. Films deposited over narrow trenches showed uniform, conformal coverage. These results demonstrate that PEALD enables high–quality $Al_{1-x}Sc_xN$ suitable for advanced three–dimensional electronic and sensing applications.

2:45pm **EM1-TuA-6 Low Temperature PEALD of Epitaxial AlN Without Atomic Layer Annealing***, **Jeffrey Woodward**, David Boris, Michael Johnson, Daniel Pennachio,* U.S. Naval Research Laboratory*; Michael Mathews,* NRC postdoctoral fellow residing at U.S. Naval Research Laboratory*; Emma Rocco,* U.S. Naval Research Laboratory*; Katie Gann,* NRC postdoctoral fellow residing at U.S. Naval Research Laboratory*; Ben Sekely,* NRC postdoctoral fellow stationed at U.S. Naval Research Laboratory*; Tatyana Feygelson, Jonathan Levine-Miles,* U.S. Naval Research Laboratory*; Jennifer Hite,* University of Florida*; Michael Mastro,* U.S. Naval Research Laboratory*; Henry Chuang,* Boston University*; Virginia Wheeler, Scott Walton,* U.S. Naval Research Laboratory

AlN is a wide-bandgap semiconductor with exceptional thermal conductivity, temperature stability, and piezoelectric properties, making it a promising material for high power and high frequency electronics, deep ultraviolet optoelectronics, and microelectromechanical systems. While AlN PEALD has been the subject of extensive research, it typically results in amorphous or polycrystalline films, which have inferior electrical properties compared to epitaxial AlN. Most reports of epitaxial AlN growth by PEALD involve the use of atomic layer annealing (ALA), in which an Ar plasma exposure is incorporated into each cycle to induce crystallization of the surface.[1] While the effectiveness of ALA is proven, its use also increases cycle duration, which significantly prolongs total process time and can promote impurity incorporation. For these reasons, the growth of epitaxial AlN without ALA is desirable, though this is challenged by the complexity of controlling the plasma properties to achieve suitable growth conditions.[2]

In this work, we demonstrate the growth of 30-50 nm thick epitaxial AlN films on Al_2O_3, GaN, and Ga_2O_3 at 300 °C using PEALD without ALA or thermal annealing. The PEALD process uses the commonly-employed combination of trimethylaluminum (TMA) and N_2/H_2/Ar plasma, and is performed in a standard commercial reactor with remote inductively coupled plasma (ICP) source.Plasma diagnostics were used to identify favorable plasma regimes which produce ion energy and flux characteristics comparable to those of plasmas used in ALA. The films were characterized using x-ray reflectivity (XRR), high resolution x-ray diffraction (HRXRD), in-plane grazing incidence diffraction (IP-GID), atomic force microscopy (AFM), transmission electron microscopy (TEM), x-ray photoelectron spectroscopy (XPS), and optical measurements. The growth per cycle (GPC) and density ranged from 0.90–1.03 Å and 2.998–3.173 g/cm^3, respectively, depending on substrate, with deposition on GaN resulting in the highest GPC and density.The topography of the films closely replicated that of the underlying material with roughness from 0.25–1 nm by AFM and 0.83–2 nm by XRR, indicating that the deposition was highly conformal. The epitaxial nature of the AlN (i.e., exhibiting a highly ordered crystalline structure with well-defined orientational relationship to the substrate) is confirmed by HRXRD and IP-GID, which show the films to be single phase and orientation with 6-fold azimuthal rotational symmetry. While the AlN films on Al_2O_3 and Ga_2O_3 are wurtzite phase with significant mosaicity, the AlN on GaN is metastable zincblende phase with low tilt disorder, as evidenced by narrow out-of-plane rocking curves with FWHM= 0.149 degrees (537 arcseconds). Results of AlN PEALD on nanocrystalline diamond (NCD) and single crystal diamond (SCD) will also be presented.

[1] H. Y. Shih et al., Sci. Rep. **7**, 39717 (2017)
[2] D. R. Boris et al., J. Vac. Sci. Technol. A **42**, 033008 (2024)

3:00pm **EM1-TuA-7 Enabling Blister-Free, Crystalline AlN Thin Films on 200 mm Si Wafers by PE-ALD Using a Microwave Electron Cyclotron Resonance Plasma Source***, **Shiv Bhudia,*** TUM School of Natural Sciences, Technische Universität München; Silicon Austria Labs GmbH, Austria*; Tai Nguyen,* Silicon Austria Labs GmbH, Austria*; Dominik Hartmann,* Evatec AG, Switzerland*; Marco Deluca, Julian Pilz,* Silicon Austria Labs GmbH, Austria

Aluminum nitride (AlN) is an important material for optoelectronics,[1] energy harvesting, and surface-acoustic-wave transducers and resonators.[2–5] It also enables devices operating at high frequencies and in thermally and chemically harsh environments.[6] This interest stems from its combination of a wide bandgap, high thermal conductivity, favorable lattice constant, and piezoelectric properties. In most applications, (002)-textured wurtzite films are required to achieve the desired device performance.[7] Furthermore, when fabricating 3D nanostructures such as microelectromechanical systems (MEMS),[8] memory devices,[9] and through silicon via (TSV) technology,[10] conformal growth and atomic-scale control are essential. Atomic layer deposition (ALD) has been proven to be an enabling deposition method under these conditions.

However, obtaining AlN films with crystal quality comparable to that of other deposition techniques remains challenging for ALD on Si substrates,[11–13] as oxygen and carbon impurities can significantly degrade crystallinity. Surface blistering is also a critical reliability issue in ALD and PE-ALD AlN,[14] yet systematic wafer-scale studies are scarce in literature. Moreover, the use of electron cyclotron resonance (ECR) plasma sources for AlN growth has received limited attention to date.[15]

In this work, AlN films are deposited on 200 mm Si(111) wafers using plasma-enhanced atomic layer deposition with trimethylaluminum (TMA) and NH_3 plasma as reactants. A novel ALD module (Evatec PEALD) is used for film deposition, employing a microwave ECR source for plasma generation. The effects of substrate temperature (200-400 °C) and plasma power (50-200 W) on film properties and blister formation are investigated. It is found that a combination of high power and substrate temperature leads to the formation of blisters on the edge region of the wafer.Applying a combination of characterization techniques, the number of blisters as a function of process parameters could be quantified (0-10 % of wafer area), and the defect formation mechanism was identified as likely caused by stress-induced effects. Fine-tuning of the substrate temperature and plasma power enables the suppression of these defects, resulting in damage-free, crystalline, and chemically pure films on 200 mm Si(111) substrates.

In a nutshell, this work presents effective mechanisms for producing PEALD AlN thin films with preferential c-axis orientation on 200 mm wafers, highlighting the importance of plasma source and parameter selection and giving insights into the suppression of film blistering effects.

Emerging Materials and Processes
Room Tampa Bay Salons 1-2 - Session EM2-TuA
ALD for 2D Materials

Moderators: Hanmei Choi, Samsung Electronics, **Christophe Detavernier**, Ghent University, Belgium

4:00pm **EM2-TuA-11 ALD Synthesis of Transition Metal Phosphides***, **Raul Zazpe**, Jhonatan Rodriguez-Pereira, Jaroslav Charvot, Milan Klikar, Filip Bures, Jan Macak,* University of Pardubice, Czechia

The ever-increasing global energy demand together with the environmental issue originated from the use of fossil fuel, has triggered an intense search for sustainable and clean energy alternatives, such us hydrogen energy, biomass and solar energy among others. In this context, a pivotal key to deliver sustainable and superior energy systems lies on the rational design and development of high-quality and cost-effective catalyst offering enhanced stability, activity and selectivity. Consequently, intense efforts have been devoted in the search and synthesis of new catalyst materials to replace the scarce and expensive traditional noble metals (e.g. Pt, Pd, Au and Ru) for energy conversion and energy storage applications.

Among the recently explored novel catalyst materials, metal phosphides (MPs) have emerged in recent years, attracting significant attention thanks to their intriguing properties [1]. In particular, transition metal phosphides (TMPs) exhibit striking properties. The moderately strong M−P bonds lend outstanding mechanical properties, high thermal stability and outstanding chemical resistance to chemical attack and oxidation in acidic and alkaline solutions. Additionally, Co, Ni, Mo-based phosphides demonstrated excellent catalytic and bifunctional properties towards water splitting as

both hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) [2,3].

Herein, we present the synthesis of TMPs by thermal Atomic Layer Deposition (ALD), including cobalt and titanium phosphide [4], based on the use of different transition metal precursors combined with in-house synthesized P precursors. The physical and chemical properties of the resulting TMPs thin films were extensively characterized by different methods, including atomic force microscopy, X-ray photoelectron spectroscopy and X-Ray diffraction. The presentation will introduce and describe the synthesis of the TMPs and the corresponding characterization toward diverse applications.

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4:15pm **EM2-TuA-12 A Novel Chemistry toward the Atomic Layer Deposition of MoS2 thin films for Heterojunction Photocatalysis**, ***Annmary Anto***, *Alexey Ganzhinov, Anjan Deb, Kenichiro Mizohata, Mykhailo Chundak, Mikko Ritala, Matti Putkonen,* University of Helsinki, Finland

Among the transition-metal dichalcogenides (TMDCs), MoS2 is the most extensively studied two-dimensional (2D) material owing to its excellent opto-electronic properties and the semiconducting nature. It is one of the most promising visible-light photocatalytic materials, recognized for potential in electronics to improve device efficiency and enhanced charge retention in energy storage. To harness these applications,researchers have explored a wide range of synthesis techniques,from top-down to bottom-up methods including exfoliation, thermal synthesis, and vapor phase deposition for the development of 2D-MoS2. However, in comparison with any other approach, atomic layer deposition (ALD) offers higher reproducibility and reliability due to its growth insensitivity towards excessive precursors.

Herein, we report a new thermal ALD process to fabricate MoS2 thin films up toa growth rate of 1.5 A°/Cycle at 200–300°C,using Mo(II) acetate dimer and H2S as Mo and S sources, respectively. As-deposited films on Si (100) with native oxide are found to be crystalline in nature, though rough, consisting of flake-like grains, and the X-ray diffraction (XRD) measurements confirmed the presence of (002) plane oriented 2H-MoS2 phase.The ALD-MoS2 films exhibited S/Mo ratio of 2.1–1.3, according to the deposition parameters, with O, C, and H impurities (<10 at.% in total) measured by time-of-flight elastic recoil detection analysis (ToF-ERDA). X-ray photoelectron spectroscopy (XPS) confirmed the formation of chemical bonding from MoS2. The crystalline nature of the films improved with a decline in conductivity along with the temperature. A transformation from in-plane to out-of-plane orientation of the two-dimensional layers as a function of number of cycles was observed.

Optical analysis indicated an energy gap ranging from 2.1 to 1.5 eV for films deposited on soda lime glass, increasing with higher S content. In addition, photocatalytic activity was demonstrated using solar sensitized methylene blue degradation. Further results on the development of heterojunction photocatalyst by integrating the developed MoS2 thin films with suitable oxides will be presented.

4:30pm **EM2-TuA-13 The Role of Plasma Conditions on the Properties of MoS_2 Films Grown by PEALD Using H_2 plasma and Di-tert-butyl Disulfide**, ***Paula Arellano,*** University of Michigan, Ann Arbor*; Ian E. Campbell,* IMEC*; Aashi Gupta, Pavlina Metaxa, Vasiliki Nousia, Ray Duffy,* Tyndall National Institute, University College Cork, Ireland*; Ageeth A. Bol,* University of Michigan, Ann Arbor

The presence of plasma species during PEALD enables film growth at temperatures lower than those usually required for thermal ALD and other deposition methods. We recently demonstrated a low-temperature PEALD process for molybdenum disulfide (MoS_2), based on $Mo(tBuN)_2(NMe_2)_2$ and di-tert-butyl disulfide (TBDS) in combination with H_2 plasma as the coreactant. TBDS is a safer and less hazardous alternative to hydrogen sulfide (H_2S) for PEALD of MoS_2 thin films.[1] Raman spectroscopy however showed that MoS_2 films grown using the TBDS process exhibit higher defect densities than those grown using a H_2S PEALD process. In this work, we study the effect of the H_2 plasma conditions on the quality of the resulting MoS_2 films and demonstrate how careful optimization of the plasma conditions (plasma power, plasma feed gas composition, pressure and flow rate) can reduce the plasma-induced damage and improve the crystallinity of the MoS_2.

The use of H_2 plasma during the TBDS process is thought to remove the Mo precursor ligands and reduce chemisorbed Mo^{6+} species to Mo^{4+} before the TBDS exposure. After characterizing the effects of H_2 plasma parameters on PEALD MoS_x, the defects-to-intensity ratio in the Raman spectra ranged from ~2.7 to ~1.0, revealing a substantial decrease in defect density for PEALD recipes with low power, high pressure H_2 plasma exposure. However, the surface roughness (R_q) of 6 nm thick MoS_x films, as measured by AFM, increased under these conditions due to out-of-plane fin growth.

To reduce fin formation in MoS_x films, we incorporated a low flow rate, low power, long duration Ar plasma step in our ALD cycle scheme. As a result, the R_q of ~6 nm thick MoS_x films decreased from 2.09 nm to 0.435 nm, while the defects-to-intensity ratio in the Raman spectra increased from 1.6 to 2.0. Thus, a tradeoff between fin growth and higher structural disorder exists when tuning the parameters of H_2 and Ar plasma exposures.

Finally, the electrical properties of MoS_x films with varying crystallinity and morphology will be compared. This work shows that the incorporation and optimization of plasma steps during PEALD of MoS_2 can further improve the quality of the resulting MoS_2, enabling the use of safer sulfur chemistry while achieving scalable, damage-controlled thin-film growth.

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4:45pm **EM2-TuA-14 ALD-Induced Doping Effect in 2D MoS_2 FETs: Roles of Oxidant Chemistry and MoS_2 Quality**, ***Minjong Lee***, *Thi Thu Huong Chu, Inhong Hwang, Doo San Kim, Dushyant Narayan, Dan Le, Soham Shirodkar, Jiyoung Kim,* University of Texas at Dallas

As scaling pushes device platforms toward three-dimensional (3D) integration, ultrathin gate dielectrics must be deposited directly on two-dimensional (2D) channels [1]. Atomic layer deposition (ALD) is a leading method for enabling such gate-stack integration. However, the surface chemistry required for nucleation can also unintentionally modulate carrier density in the 2D channel [2]. In MoS_2 field-effect transistors (FETs), this deposition-induced “atomic-layer doping (ALDo)” can alter key device metrics in ways that are often difficult to separate from nucleation-driven interfacial reactions and trap generation.

This work presents an *in-situ*/*ex-situ* characterization framework to track MoS_2 device evolution throughout the ALD gate-dielectric process. *In-situ*, we monitor electrical changes associated with individual ALD half-cycles to capture the initial deposition-induced shifts. *Ex-situ*, we quantify net performance evolution after dielectrics growth to few-nanometer thicknesses. Across ALD cycles, the most pronounced performance changes occur in the initial-growth regime, indicating that interfacial reactions dominate the ALDo response. MoS_2 film quality further sets the baseline sensitivity to ALDo. Exfoliated single-crystal MoS_2 exhibits minimal performance perturbation following few-nanometer gate-dielectric formation, whereas chemical vapor deposition (CVD)-grown MoS_2 shows clear degradation, implicating stronger interfacial reactions. Oxidant chemistry further modulates device behavior: O_3 tends to induce more severe surface perturbation, while H_2O_2 can promote S-O bond formation and yield qualitatively improved electrical characteristics.

Building on these insights, we outline practical routes toward quasi-single-crystal-like behavior in CVD-grown MoS_2 films by scaling channel length to confine transport within a single grain with suppressing excessive oxidation in the defect states. This study demonstrates a device-level diagnostic that accelerates mechanism-guided optimization of ALD gate stacks on 2D channels. The presentation will cover the measurement methodology, integration strategies, and prototype workflows for engineering ALDo, with implications for reliable 2D-FET operation toward future 3D-integrated electronics.

This work was supported by Samsung Electronics through GRO program (IO250621-13116-01) and the KEIT grant funded by MOTIE (RS-2023-00235484, No, 1415187770). The ozone generator was provided by TMEIC, and the BRUTE® Peroxide was provided by RASIRC Inc.

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5:00pm **EM2-TuA-15 Processing MoS_2 and WS_2 using ALD and Patterning on 8-Inch Wafers**, ***Nils Boysen***, *Leon Doman, Rahel-Manuela Maas, Anjana Devi,* Fraunhofer IMS, Germany

Processing 2D materials using various deposition and patterning methods on larger wafer scales is a major challenge in developing next-generation devices, such as ultra-sensitive sensors for photo-, gas-, and biosensing. In particular, ultra-thin films of layered 2D materials such as MoS_2 and WS_2 exhibit promising properties for sensing applications due to their semiconducting nature, high surface-to-volume ratio, and intrinsic selectivity for different analytes. One of the main challenges to date is the deposition and subsequent patterning of such delicate layers on larger areas, such as 8" silicon wafers. Because of their high sensitivity to oxidation and delamination, standard patterning routes cannot be readily adopted. Typically, MoS_2 and WS_2 are exfoliated and transferred to the target substrates. However, this top-down route adds a significant number of processing steps and is not easily scalable to larger scales. Furthermore, the layers must be on the uppermost layers of the device stack to be accessible for sensing applications, which rules out thick protective capping layers typically used in such stacks.

To overcome these challenges, we introduce a feasible approach to deposit MoS_2 and WS_2 via bottom-up ALD as the uppermost layer on pre-structured metallization layers. Subsequently, we enable patterning of MoS_2 and WS_2 via lithography and ion-beam etching, using in situ ALD Al_2O_3 capping layers that can be later porosified for sensing applications. Accordingly, we developed an ALD process at low deposition temperatures of 100 °C for MoS_2, and at higher deposition temperatures of 350 °C for WS_2 using $[Mo(NMe_2)_4]$, $[W(NtBu)_2(NMe_2)_2]$, and H_2S as precursors (Fig. 1). This resulted in ultra-thin layers that were amorphous for MoS_2 and crystalline with a 2D layered structure for WS_2. Subsequent patterning of the MoS_2 and WS_2 by photolithography and ion-beam etching (IBE) with the help of in-situ deposited Al_2O_3 capping layers prevented delamination and severe oxidation of the amorphous and crystalline layers, as proven by Raman spectroscopy and transmission electron microscopy (TEM) (Fig. 2) of the resulting structures. The integrity of the layers was preserved after porosifying the Al_2O_3 capping layer in boiling water, enabling sensing applications (Fig 3). In the case of patterned MoS_2, selective gas-sensing of relevant gases such as NO_2, NH_3, and H_2S could thus be achieved.

In summary, the new and promising developments in bottom-up 2D material processing via ALD have enabled us to realize sensing structures at a larger wafer scale and will facilitate the adoption of these materials for other device applications.

5:15pm **EM2-TuA-16 Exploiting Atomic Layer Deposition for Contacts to Semiconductors**, ***Suzanne Mohney***, *Chan-Wen Chiu, M. Saifur Rahman, Ryan Wang, Sree Palaniappan,* Pennsylvania State University

Electrical contacts to semiconductors in transistors and other electronic devices are typically formed by physical vapor deposition techniques such as sputtering or evaporation. Atomic layer deposition (ALD), however, offers unique opportunities for engineering electrical contacts across a wide range of semiconductor families. For example, we previously used an ultrathin ALD-grown dielectric to reduce the metal/semiconductor Schottky barrier height and achieve low-resistance ohmic contacts to silicon [1]. We also compared thermal ALD [2] and remote–plasma ALD [3] processes for depositing conductive films on gallium nitride, producing high-quality Schottky diodes. Most recently, we employed ALD for hole injection in source-drain contacts to the two–dimensional (2D) semiconductor WSe_2, motivated by the promise of 2D semiconductors for device scaling and integration with silicon platforms. Achieving low contact resistance for *p*–channel 2D field effect transistors is often challenging, but we obtained a contact resistance of 10 kΩ·μm [4] using semimetallic TiS_x contacts with MoO_x capping. The TiS_x was grown by thermal ALD from tetrakis(dimethylamido)titanium and hydrogen sulfide at 100 °C. Because contact yield was impacted by nonuniform coverage of TiS_x on WSe_2, we are investigating remote-plasma ALD processes to improve nucleation of TiS_2 on WSe_2 and are examining the interplay between deposition parameters and device performance. The presentation will conclude with an analysis of the outlook for using ALD for contacts to semiconductors across technologies. The authors acknowledge support from the National Science Foundation (NSF) through ECCS 2227346. WSe_2 epilayers were provided by the Penn State 2D Crystal Consortium–Materials Innovation Platform (2DCC-MIP) under NSF DMR 2039351.Any opinions, findings, and conclusions or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of the National Science Foundation.

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ALD Applications
Room Tampa Bay Salons 5-9 - Session AA-TuP
ALD Applications Poster Session

AA-TuP-1 Improving the Thermoelectric Properties of ALD Synthesized Thermoelectric Thin Films Sb_2Te_3 by Cr+ and Ar+Ion Implantation, ***Sadiya Tahsin***, *Helmut Baumgart,* Old Dominion University

Atomic layer deposition (ALD) provides atomic-scale thickness control and excellent conformality, enabling the integration of thermoelectric materials onto complex, high–aspect ratio architectures. In this study, Sb_2Te_3 thin films were deposited by ALD on planar and porous silicon substrates and subsequently modified through ion implantation to independently tune electrical and thermal transport. Chromium (Cr^+) and argon (Ar^+) ions were employed to decouple chemical doping from structural disorders. Cr^+ implantation was used to adjust carrier concentration through electrically active doping, while Ar^+ implantation introduced lattice defects and disorder without chemical substitution. Post-implantation annealing at 225 °C enabled partial defect recovery and dopant activation. Hall effect measurements reveal a substantial increase in carrier concentration and electrical conductivity in annealed, implanted films compared to pristine as-deposited samples. This enhancement is accompanied by reduced carrier mobility, consistent with increased carrier scattering from implantation-induced defects. These results demonstrate that combining ALD-enabled conformal growth with controlled ion-beam defect engineering offers a scalable pathway for optimizing Sb_2Te_3 thermoelectric thin films through independent control of electronic and phononic transport.

AA-TuP-2 A New Sn-based Precursor as Dry Photoresist for Extreme Ultraviolet Lithography Process , ***Junsok Choi***, *Shijin Song, Youngwon Kim, Juhyung Lee, Ahreum Kim, Seonghan Kim, Dae Won Ryu,* Hansol Chemical, Republic of Korea

Extreme Ultraviolet Lithography (EUVL) has become essential process for reduction in device dimension. Recently, in EUVL, Dry-deposition & Dry-development approaches have attracted considerable attention because of their capability of preventing pattern collapse, relaxing Resolution-Line edge roughness-Sensitivity (RLS) trade-off, and reducing environment effect. As Photoresists (PR) for Dry EUVL, Sn-based precursors with EUV-sensitive ligands have been widely researched due to high absorption coefficient of Sn towards EUV light.

In this study, we developed a new Sn precursor as a dry PR for EUVL. The thin PR films of 25 nm were deposited through chemical vapor deposition (CVD). Then, 5X5 μm^2 patterns and 1:1 line/space (L/S) patterns were formed through E-beam lithography process for measurement of sensitivity resolution and line-edge roughness (LER) of the developed dry PR.

The sensitivity of the dry PR was evaluated with E-beam dose when thickness after development reaches maximum with increasing the dose for 5X5 μm^2 patterns. The thickness of those patterns after development were measured through optical microscopy. D_{100} (Dose at maximum thickness) of the PR was 399 $\mu C/cm^2$ at the voltage of 100 kV.

1:1 L/S patterns with half pitch = 50, 40, 30, 20, and 10 nm were observed with scanning electron microscopy (SEM). From hp = 50 nm to hp = 20 nm, no major defects (pattern collapse, bridging and line pinching) was observed. LER at hp =20 nm measured with Lacern program was only 1.66 nm. These results showed that our developed dry PR has satisfactory performances to realize ultra-fine nano-patterns for reducing dimension of semiconductor devices.

AA-TuP-3 Development of Air-stable Liquid Niobium Precursor with Organic-inorganic Hybrid Ligand for Conformal Atomic Layer Deposition of Nb_2O_5, ***Sun Young Baik***, *Sangbum Han,* EGTM, Republic of Korea

Metal halide precursors are widely used in Atomic Layer Deposition (ALD) and Chemical Vapor Deposition (CVD) due to their high reactivity with common oxygen sources and exceptional thermal stability. These characteristics enable excellent conformality and often produce high-purity films with lower carbon and oxygen contamination compared to many organometallic precursors. However, despite their effectiveness, a notable limitation is that most metal halides exist in the solid phase, which complicates precursor delivery and necessitates the use of specialized canisters. Additionally, corrosive reaction byproducts (e.g., HF, HCl) can damage ALD chamber components. To address these limitations, we developed a novel niobium (Nb) precursor by combining halide and organic ligands. This new Nb precursor synergizes the advantages of both ligand types; it retains the reactivity of halides while exhibiting exceptional air stability and existing in the liquid phase at room temperature. Notably, the precursor demonstrated excellent properties during the deposition process. Its liquid state facilitates stable delivery, and its superior thermal stability allows for deposition at higher temperatures. Consequently, the precursor was confirmed to achieve perfect step coverage (~100%) on patterned wafers, comparable to that of conventional metal halide precursors. We expect this new Nb precursor to be a suitable candidate for the ALD of Nb2O5 interfacial oxide layers.

AA-TuP-4 ZnO Thin Film Transistor-Based Hydrogen Sensor Fabricated by Atomic Layer Deposition, *Kaito Otsuka, Kyosuke Nakazawa, Ryo Miyazawa, Masanori Miura, Bashir Ahmmad,* ***Fumihiko Hirose***, Graduate School of Science and Engineering, Yamagata University, Japan

Hydrogen sensors are crucial devices for securing hydrogen based power generation systems. As the conventional technologies, palladium nanoparticle films were used as measuring its resistance as the H_2 signal. Moreover, the transparent oxide semiconductors such as ZnO were used as the sensing resistor for hydrogen. On the other hand, thin–film–transistor (TFT)–based sensors are attracting increasing attention because a TFT matrix can be used as a two–dimensional sensing platform. In the present study, ZnO–based TFT sensors were fabricated by atomic layer deposition to explore their potential for hydrogen detection.

In Fig. 1, the schematic of the TFT is illustrated. A nanometer–thick (12 nm) ZnO film was used as the channel layer, and the thickness was minimized to enhance the sensitivity. The ZnO film was deposited by room–temperature atomic layer deposition. The deposition system is shown in Fig. 2. The precursors were dimethylzinc and plasma–excited humidified argon. The deposition temperature was room temperature. The film was then annealed in dry air at 450°C for 30min to promote crystallization. In this TFT, the channel length and width were 60μm and 1mm, respectively.

For the hydrogen sensing test, we measured the time variation of the drain current with gate and drain voltages of 0 and 20V, respectively. The hydrogen partial pressure was increased stepwise from 200 to 6400Pa. The drain current clearly increased with increasing partial pressure, although no saturation was observed. It was also confirmed that the slope of the drain–current response correlated with the partial pressure, suggesting the applicability of the present device as a hydrogen sensor. We assume that hydrogen molecules were adsorbed on the palladium oxide, dissociated into atomic hydrogen, and diffused into the ZnO channel, where the enhanced carrier conduction led to the steep increase in drain current.

At the conference, we will discuss the operation mechanism together with more detailed experimental results.

AA-TuP-5 Titanium Nitride Protective Coatings for High-Performance Proton Exchange Membrane Water Electrolysis, ***Bhavesh Chavan***, *Ruud Kortlever, Ruud van Ommen,* Delft University of Technology, Netherlands

Proton-exchange membrane (PEM) water electrolysis is a leading technology for green hydrogen production, offering high efficiency and compact design. However, its widespread adoption is hindered by the reliance on costly platinum group metals and titanium-based components required to endure the acidic, oxidizing environment during operation [1].

Titanium-based components, such as the porous transport layer (PTL) and bipolar plates, play critical roles in facilitating mass transport, ensuring uniform current and heat distribution, and providing mechanical stability to the system. Yet, under operational conditions, these components form semiconducting oxide layers, which reduce electrical conductivity and compromise system efficiency. Additionally, they require high hydrophilicity to improve gas-liquid contact and mass transfer. To address these challenges, these components are often coated with thick layers (~200nm) of precious metals such as platinum or gold, increasing costs significantly [2].

In this work, titanium nitride (TiN) coatings are investigated as a cost-effective alternative to conventional Pt or Au coatings on PTLs, aiming to provide high corrosion resistance, conductivity, and hydrophilicity [3,4]. Three gas-phase coating techniques to make TiN are explored in this work: atomic layer deposition (ALD), reactive sputtering (physical vapor deposition), and direct plasma nitridation. ALD offers excellent coating conformality and high penetration depth but involves a more complex and time-intensive process. In contrast, reactive sputtering is a simpler and more cost-effective method, though it can compromise coating conformality. The conformality achievable with direct plasma nitridation remains uncertain and requires further evaluation.

Initial studies involved TiN film deposition on silicon wafers to evaluate coating quality, followed by application on 3D PTL structures. Electrochemical testing was first conducted in a three-electrode setup, after

which the coated PTLs were evaluated under PEM water electrolysis conditions. The results of our work demonstrate the potential of titanium nitride coatings as a scalable protective layer for PEM water electrolysis components, offering a pathway toward cost-effective and efficient green hydrogen production.

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AA-TuP-6 Controlled Interface Oxidation of Ru/RuO_2 Thin Films Through High Concentration H_2O_2 Exposure*, **Austen Adams,** Dan Le,* RASIRC

The modern trend of semiconductor device design approaching increasingly smaller scales, alongside the desire for devices to be integrated into complex three-dimensional architectures, has caused an industry-wide need for precise control over film quality and interface properties. The interface between bottom electrode materials and dielectric layers is of particular interest as the thickness of a modern dielectric decreases to the single nanometer range. Ru is a well-studied bottom electrode material for dynamic random-access memory applications, in part due to its low bulk resistivity (7.1 μΩ cm) and high work function (4.7eV). Unfortunately, during oxidation cycles of dielectric ALD the industry standard O_3 exposure often causes the formation of volatile RuO_4. The result of this oxidation effect being lower quality Ru-based interfaces with etched RuO_2. In previous semiconductor generations this surface roughness for a bottom electrode interface would be a minor concern, but as modern semiconductor designs demand thinner films, the need for a higher quality and uniform interfaces has become pertinent.

Here we showcase evidence of higher quality uniform RuO_2 thin film formation via BRUTE Peroxide (high concentration H_2O_2)exposure, mitigating the formation of RuO_4. We compare these films to comparable O_3 exposed Ru/RuO_2 films and as-deposited Ru films. Resulting structures are characterized through scanning electron microscopy surface imaging, x-ray reflectivity and x-ray photoelectron spectroscopy analysis, among other techniques.

AA-TuP-7 Plasma-Enhanced Atomic Layer Deposition of Niobium Nitride Using a New Nb Precursor and Its Application to Diffusion Barriers for Cu and Ru Interconnects*, **Kyungmin Kim,*** Department of Energy and Chemical Engineering, Ulsan National Institute of Science and Technology (UNIST), Republic of Korea*; Chaehyun Park, Minjeong Kweon,* Graduate School of Semiconductor Materials and Devices Engineering, Ulsan National Institute of Science and Technology (UNIST), Republic of Korea*; Yongjoo Park, Donghyun Kim,* Advanced Reasearch Development Team, SK Trichem Co. Ltd., Sejong, 30068, Korea*; Soo-Hyun Kim,* Graduate School of Semiconductor Materials and Devices Engineering, Ulsan National Institute of Science and Technology (UNIST), Department of Materials Science and Engineering, Ulsan National Institute of Science and Technology (UNIST), Republic of Korea

Continued scaling of semiconductor interconnects has led to increased RC delay, reduced Cu volume, size-effect-induced resistivity increase, and degraded electromigration reliability. Conventional Cu interconnects rely on complex TaN/Ta diffusion barrier and liner stacks. However, this multilayer scheme faces severe scaling limitations, thereby motivating the search for alternative diffusion barrier and liner materials. Transition-metal nitrides (TMNs) especially niobium nitride (NbN) offer high melting point (≈2400 °C), strong chemical stability, and metallic conductivity (58–78 μΩ·cm), making them suitable diffusion barrier candidates for advanced interconnect integration [1] [2]. As interconnect dimensions continue to shrink, atomic layer deposition (ALD) becomes essential due to its self-limiting surface reactions, excellent conformality, and precise thickness control in high-aspect-ratio device structures. In this study, we investigate the ALD feasibility of NbN_x thin films using a novel liquid Nb precursor, which offers higher volatility and stable vapor delivery compared with conventional solid precursors such as $NbCl_5$ or NbF_5. Multiple reactants including NH_3 molecule, NH_3 plasma, N_2 plasma, and N_2:H_2 mixture plasma were examined to identify effective nitridation pathways. Among them, NH_3 plasma was the only reactant capable of forming crystalline NbN_x and further experiments were done mainly using NH_3 plasma. The ALD-NbN_x process was conducted in a showerhead-type PEALD reactor (IOV dX1 PEALD, ISAC RESEARCH, Korea). Self-limiting growth behavior was confirmed through both precursor and reactant pulsing time, with a saturated growth rate of approximately 0.18 Å/cycle. A stable ALD temperature window was identified between 250–350 °C, with the best film quality achieved at 300 °C. The properties of ALD-grown NbN_x films were characterized using XRD, XRR, SEM, XPS and TEM. Finally, the ALD-grown NbN_x films were evaluated as diffusion barrier for Cu and Ru interconnects, demonstrating their potential for advanced interconnect applications. Detailed barrier performance results will be presented at the conference.

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Acknowledgements

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AA-TuP-8 Ultrathin Sn-Doped In_2O_3 Films for Scalable Semiconductor Transistors*, **Seung Ho Ryu,** Seong Keun Kim,* Korea University, Republic of Korea*; Taikyu Kim,* Stanford University, Republic of Korea*; Taeseok Kim,* Korea University, Republic of Korea

As transistor scaling progresses, ultrathin channel structures are increasingly required to suppress short-channel effects and enhance gate control in advanced device architectures such as FinFETs and gate-all-around (GAA) transistors. However, reducing channel thickness typically leads to severe degradation in conductivity, limiting the electrical performance of thin-film transistors (TFTs). In this study, we investigate an ultrathin Sn-doped In_2O_3 (ITO) channel to overcome this challenge. The uniform Sn doping enhances carrier density and mitigates the conductivity degradation associated with ultrathin channels, ensuring stable electrical performance. As a result, we successfully fabricate enhancement-mode TFTs with a 1.5 nm-thick ITO channel, achieving a high field-effect mobility of 33.4 ± 1.5 cm^2/V·s, a subthreshold swing of 129 ± 30 mV/dec, and a threshold voltage of 0.3 V. These findings provide a crucial strategy for realizing high-performance oxide TFTs with ultrathin conducting channels, addressing a key challenge in the development of next-generation semiconductor devices.

AA-TuP-9 A Film-Quality-Aware ALD Integration Framework for Top-Gated MoS_2 FETs*, **Minjong Lee,** Thi Thu Huong Chu, Inhong Hwang, Doo San Kim, Dushyant Narayan, Dan Le, Soham Shirodkar, Jiyoung Kim,* University of Texas at Dallas

Top-gated MoS_2 FETs require conformal, ultrathin high-k dielectrics with low interface trap density [1]. However, the surface-limited reactions in atomic layer deposition (ALD) can also perturb MoS_2 channel chemistry, degrading electrostatic control and limiting reproducibility [2]. It is thus critical to establish a process-channel framework that decouples nucleation-driven interface formation from channel-damaging reactions. In this work, we examine how MoS_2 film quality governs top-gate insulator integration and defines the boundary between chemistry-enabled interface improvement and defect-activated channel damage.

We first established a single-crystal benchmark using mechanically exfoliated few-layer MoS_2. Comparative oxidant studies show that H_2O_2-based ALD of HfO_2 yields improved gate controllability relative to conventional oxidants (H_2O, O_3), consistent with a chemically stabilized interface associated with S-O bond formation. These results indicate that oxidant engineering can overcome the conventional nucleation-interface-quality tradeoff without relying on seed or interfacial-layer strategies, providing a practical route for scaled top-gated 2D devices.

We then extend the same gate-stack process to wafer-scale MoS_2 films from multiple sources (e.g., chemical vapor deposition (CVD)- and chemical vapor transfer (CVT)-grown). In contrast to exfoliated single-crystal flakes, large-area MoS_2 exhibits overall degradation after high-k deposition, indicating that film non-idealities and spatial variability dominate the integration outcome. We attribute this divergence to defect-mediated interfacial chemistry, where abundant reactive sites in wafer-scale MoS_2 promote localized oxidation and non-ideal bonding even under H_2O_2-

enabled deposition, thereby degrading transport and gate controllability. This trend further suggests that defective MoS_2 films require milder ALD windows (e.g., lower temperature and reduced oxidant reactivity) to suppress defect-activated parasitic reactions while preserving nucleation.

Overall, this study establishes process-structure-property relationships linking MoS2 quality to top-gate dielectric integration and provides actionable design rules for reliable 2D FET gate stacks toward future 3D-integrated electronics.

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AA-TuP-10 Atomic Layer Deposition of Pt on Plasma-Activated Tungsten Oxide Support for Durable PEMFC Anodes, ***Hyung Jong Choi***, Stanford University; *Hae Wook Park, Beum Geun Seo, Jung Woo Shim, Nam Il Kim, Yun Sung Choi,* Korea University, Republic of Korea; *Fritz B. Prinz,* Stanford University; *Joon Hyung Shim,* Korea University, Republic of Korea

Atomic layer deposition (ALD) can provide a unique pathway to maximize the utilization of noble metal catalysts by controlling the distribution and loading at the nanoscale. This study fabricated Pt nanoparticles on WO3 support using plasma-enhanced ALD (PEALD) to develop a high-performance anode catalyst for polymer electrolyte membrane fuel cells (PEMFCs) operated under fuel starvation conditions. Prior to Pt deposition, the surface of the WO3 support was treated by Ar plasma to generate oxygen vacancies and enhance the electrical conductivity of the support. The surface treatment could accelerate Pt island formation on the WO3 surface, which is driven by activation of the WO3 surface. The resulting Pt–WO3 interface could enhance hydrogen spillover and form HxWO3 species, which can act as a temporary proton–electron buffer via reversible decomposition, which is helpful in fuel starvation situations. The species also helps consume intruding oxygen during start-up/shutdown, thereby stabilizing the anode potential. As a result, the resulting catalyst platform fabricated by Ar plasma treatment and the subsequent PEALD Pt process showed enhanced stability compared to commercial Pt/C across multiple harsh protocols, including fuel-starvation transients.

AA-TuP-11 Impact of Mid-Interlayer Insertion on the Ferroelectric Performance Enhancement of $Hf_{0.5}Zr_{0.5}O_2$ Thin Films through Remote Plasma ALD, ***MinGyun Kang***, *HyeonWu Nam, YongWoon Jang, ByungWook Kim, ChangYun Hong, JiWon Kim, ChangBun Yoon,* Department of Advanced Material Engineering. Tech University of Korea., Republic of Korea

Ferroelectric HZO is a promising candidate for next-generation memory. However, stabilizing the ferroelectric orthorhombic phase (o-phase) while suppressing the monoclinic phase remains a challenge in ultra-thin films. Furthermore, leakage current and reliability issues, such as wake-up effects and retention loss in Metal-Ferroelectric-Metal (MFM) structures, require advanced interface engineering strategies. This study investigates the impact of mid-interlayer (Mid-IL) insertion (SiO2,TiO2, and Al2O3) on the performance of HZO films fabricated by remote plasma ALD (RP-ALD). Metal-Ferroelectric-Metal (MFM) capacitors were fabricated on highly doped n++ Si wafers. A 50-nm-thick TiN bottom electrode was deposited via thermal ALD. Subsequently, HZO films were deposited using a plasma-enhanced ALD system in a 1:1 super-cycle scheme of Hf and Zr precursors. RP-ALD was performed with a high plasma power of 2600W to ensure high-quality film densification while minimizing plasma-induced damage. An asymmetric HZO(2nm)/Interlayer(1nm)/HZO(7nm) stack was specifically designed to optimize phase evolution. In this structure, the 2-nm bottom HZO acts as a seed layer influenced by the TiN electrode, while the interlayer effectively promotes o-phase crystallization in the upper 7-nm HZO. A 50-nm-thick TiN top electrode was sputtered, followed by post-metallization annealing (PMA) at 400-700°C. The electrical characterization reveals that the insertion of a mid-interlayer significantly influences the crystallization kinetics and phase evolution of the HZO films. Moreover, the bandgap engineering provided by the 1nm insulating interlayer contributed to a substantial reduction in leakage current density by blocking the charge carrier transport paths. Consequently, the engineered HZO/IL/HZO capacitors demonstrated remanent polarization (2Pr) of 20-25 $\mu C/cm^2$ and a significantly suppressed leakage current density of ~ 10^{-8} A/cm^2, along with enhanced breakdown voltage, superior reliability characteristics, including stable retention compared to the single layer HZO counterparts. This study suggests that mid-interlayer engineering, combined with the low-damage RP-ALD process, is a viable solution for optimizing the performance of HZO-based ferroelectric memory devices. This work was supported by K-CHIPS(Korea Collaborative & High-tech Initiative for Prospective Semiconductor Research) (2410011219, RS-2023-00237030, 23027-15FC) and by the Technology Innovation Program (Materials & Components Technology Development (R&D)– Package-type) (RS-2025-02220734, Development of Manufacturing Technology for High-Purity iron chloride (>99.5%) and Sodium Silicate (>97.0%) via Utilization of Bayer Process Byproducts) funded By the Ministry of Trade Industry & Energy(MOTIE, Korea).

AA-TuP-12 High-quality CeO_2 thin films by low temperature atomic layer deposition using a new heteroleptic Ce precursor, ***Juri Kim***, *Yewon Seo, Soo-Hyun Kim,* Ulsan National Institute of Science and Technology (UNIST), Republic of Korea

Cerium oxide (CeO_2) is a rare-earth oxide with a high dielectric constant, moderate bandgap, excellent chemical stability, and multiple valence states (Ce^{3+}/Ce^{4+}). Owing to these properties, CeO_2 has been widely investigated for applications such as CMOS gate dielectrics, SOFCs, gas sensors, and resistive switching memories. The formation of CeO_2 requires complete oxidation of Ce^{3+} to Ce^{4+}, which demands a relatively high oxidation potential. However, under low-temperature ALD conditions,the limited oxidation capability of conventional O_2- and H_2O-based oxidants often results in degraded film quality due to incomplete oxidation and residual organic species.To overcome these limitations, O_3 was selected as the oxidant in this study. Ozone (O_3) generates highly reactive oxygen species upon decomposition, providing strong oxidation capability and enabling effective low-temperature oxidation without plasma assistance. In this work, CeO_2 films were deposited by ALD (IOV dX1 PEALD reactor, ISAC Research, Korea) using aheterolepticcyclopentadienyl-amidinate Ce precursor and O_3 as the reactant. As shown in Figure 1, CeO_2 films deposited using O_3 exhibit stronger diffraction peaks than those grown with conventional oxidants (H_2O, O_2, and O_2 plasma), indicating improved crystallinity. The deposition temperature was conducted at temperatures ranging from 150 to 350 °C, with 200 °C determined as the optimal growth temperature. The self-limiting growth behavior was shown with both precursor pulsing and reactant pulsing and the saturated growth-per-cycle (GPC) was approximately 1.15 Å/cycle. Film properties varied with deposition conditions and were characterized by SEM (thickness), TEM (step coverage, thickness), XRR (density and thickness), XRD (crystallinity), XPS (composition) and RBS (impurity). Electrical properties were evaluated via Metal–Oxide–Semiconductor capacitors, focusing on dielectric constant and leakage current. The detailed results will be presented at the conference.

Acknowledgements

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AA-TuP-13 Drain-Current-Enhanced TiO_2-Thin-Film Transistors Fabricated by Atomic Layer Deposition, ***Ryo Miyazawa***, *Tsubasa Takami, Masanori Miura, Bashir Ahmmad, Fumihiko Hirose,* Graduate School of Science and Engineering, Yamagata University, Japan

Nanometer-thick TiO_2-channel thin-film transistors (TFTs) are promising not only as high surface-sensitive sensors but also as active-matrix switching devices. InGaZnO (IGZO) has been used as a high-mobility TFT channels, offering around 10 cm^2/Vs. However, IGZO includes rare metals such as indium and gallium, leading to issues related to high cost geopolitical risks. On the other hand, TiO_2 is abundant on earth, non-toxic, although the field effect mobility of TiO_2-TFT was reported to be low due to defects in the film. In this study, the drain current enhanced TiO_2 TFTs were developed using atomic layer deposition.

We fabricated TiO_2-TFTs with a channel thickness of 16 nm as shown in Fig. 1, in which the channel surface was covered with an aluminum-silicate and SiO_2 periodical stacks. The stack layer serves as both the alkali metal absorber in the chloride solution and the meal diffusion source. The TiO_2 channel was deposited by atomic-layer deposition, followed by being annealed in dry air to induce crystallization. TFT samples were immersed in the alkali metal chloride solution, and it was assumed that the adsorbed

metals were automatically diffused to the channel layer, which might contribute to deactivating the defects in the channel layer.

We confirmed the enhanced drain currents with CsCl and NaCl solutions as shown in Fig. 2. This suggests their potential as a high-mobility TFT. The effective mobility was calculated to be 83 and 46 cm^2/Vs for Cs and Na, respectively. XPS measurements suggested a reduction of TiO_2, which might contribute to the deactivation of the Oxygen-deficiency-related defects in the TiO_2 channel layer. In the conference, we shall discuss the current enhancement mechanism and applicability as an active-matrix switching devices.

AA-TuP-14 Exploring Dopant Candidates to Improve the Electrical Properties of TiO_2 Dielectric Thin Film, ***Seungwoo Lee***, *Gaeul Kim,* Kyung Hee University, Republic of Korea*; Hansol Oh, Hanbyul Kim, Donghun Shin, Yongjoo Park,* SK trichem, Republic of Korea*; Woojin Jeon,* Kyung Hee University, Republic of Korea

Dynamic random-access memory (DRAM) has been continuously scaled down to reduce production costs and increase integration density, thereby reducing the area occupied by cell capacitors and decreasing cell capacitance. This decrease in cell capacitance reduces sensing margin in read operations. Therefore, a material with a higher dielectric constant (*k*) is required as an insulator in DRAM capacitors to recover cell capacitance. TiO_2 in the rutile phase is an attractive candidate due to its high *k* value (>100) and compatibility with atomic layer deposition. However, it has leakage current issues due to its small bandgap (~3 eV). Therefore, suppressing leakage current via conduction band offset control between TiO_2 and the electrode film, such as Al doping, was effective. However, Al doping significantly decreases the capacitance density of TiO_2.

In this work, we evaluated the effectiveness of Mg, Sc, Gd, and In as alternative dopants for replacing Al. Crystallinity of each doped TiO_2, as a function of dopant and concentration, was analyzed by grazing-incidence X-ray diffraction, and the trend was consistent with dopant formation energy results obtained from density functional theory (DFT)-based simulations. Additionally, we evaluated the electrical properties of each doped TiO_2 and elucidated the dopant-dependent mechanism of electrical properties changes using X-ray photoelectron spectroscopy analysis and DFT simulations. Consequently, the Sc dopant did not significantly degrade the dielectric constant of TiO_2 among dopant candidates, thereby further improving the electrical properties by controlling the Sc doping concentration gradient.

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AA-TuP-15 Leakage suppression and memory window optimization via Gd-doped HfO_2 charge-trap layers in 3D NAND, ***Lee Jonghyeok***, *Jeon Woojin,* Kyung Hee University, Republic of Korea*; Nam Jihun,* Kyung Hee university, Republic of Korea*; Oh Hansol, Kim Hanbyul, Park Yongjoo,* SK trichem, Republic of Korea

Three-dimensional NAND (3D NAND) memories demand charge-trap stacks that provide wide memory windows at low programming voltages for reliable multi-level cell operation and reduced cell-to-cell interference. Hafnium oxide (HfO_2) has emerged as a promising charge-trap layer material because of its high dielectric constant and strong trapping capability.[1]However, uncontrolled intrinsic defects and non-uniform trap distributions in pristine HfO_2 often lead to leakage current and unstable charge storage.

To address these issues, previous studies have reported that Gd doping was employed to engineer the trap characteristics of HfO_2.[2]The substitution of Hf^{4+} by Gd^{3+} induces local lattice distortion and defect complexes, which suppress shallow oxygen-vacancy-related traps and generate energetically deeper trap states. These deep traps enhance charge confinement and suppress leakage pathways, resulting in an enlarged memory window and improved retention characteristics.

In this work, $Al_2O_3/HfO_2/Al_2O_3$ capacitors with Gd-doped HfO_2 layers (1–10%) were fabricated and evaluated using incremental step pulse programming. The 5% Gd-doped HfO_2 stack exhibited the widest memory window and the most efficient programming behavior, indicating an optimal deep trap density for charge storage. Electrical measurements further revealed that Gd doping improves the blocking characteristics by reducing leakage current, thereby enhancing charge retention performance.

Post-metallization annealing at 400 °C significantly modified the trap distribution, promoting the formation of deeper trap states and improving programming efficiency. In contrast, excessive Gd doping (≥10%) led to degraded hysteresis behavior, suggesting leakage-dominated transport due to excessive defect generation.

These results demonstrate that Gd-induced deep trap engineering, combined with thermal processing, provides an effective strategy for optimizing HfO_2-based charge-trap stacks, enabling low-voltage, wide-window, and high-reliability operation for future 3D NAND flash memory applications.

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AA-TuP-16 Leakage Current Suppression at Grain Boundary in Rutile TiO_2 via La Doping, ***Gaeul Kim***, *Seungwoo Lee,* Kyung Hee University, Korea (Democratic People's Republic of)*; Hansol Oh, Hanbyul Kim, Donghun Shin, Yongjoo Park,* SK Trichem Co., Ltd., Korea (Democratic People's Republic of)*; Woojin Jeon,* Kyung Hee University, Korea (Democratic People's Republic of)

As dynamic random-access memory (DRAM) devices continue to scale down, the reduction of equivalent oxide thickness in cell capacitors has become increasingly critical, necessitating the use of high-k dielectric materials. Rutile-phase TiO_2 is a representative high-k material with dielectric constant of approximately 100 or higher; however, its relatively narrow bandgap and donor levels associated with oxygen vacancies lead to high leakage current. Therefore, acceptor doping using trivalent cations, particularly Al, has been investigated as an approach to reducing leakage current.

In this study, we propose a new approach to effectively suppress leakage current through grain boundary in TiO_2. Grain boundary is defect-rich regions where electron accumulation can readily occur, thereby acting as leakage current conduction paths. To suppress leakage current through grain boundary, La was doped to induce segregation toward grain boundary. Because La^{3+} has a larger ionic radius than Ti^{4+}, its substitution into the TiO_2 lattice is limited, and this significant ionic radius mismatch can promote preferential segregation of La at grain boundary. After La doping, post-deposition annealing (PDA) was performed to induce La segregation. Grazing-incidence X-ray diffraction analysis revealed that the rutile TiO_2 peak shifted toward higher angles after PDA at 600 °C compared to the as-deposited state. This shift indicates a reduction in the d-spacing of TiO_2 as La initially present within the lattice migrated to grain boundaries during annealing, supporting the occurrence of La grain boundary segregation. Furthermore, electrical characterization showed a significant reduction in leakage current in La-doped TiO_2 dielectrics, which is attributed to the effective suppression of grain-boundary-related conduction paths. These results suggest a novel mechanism for reducing leakage current in rutile TiO_2-based high-k dielectrics and provide a promising approach for next-generation DRAM capacitor applications.

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AA-TuP-17 Development of Si-C-Si Bond-Containing Precursors for SiOC Thin Films, ***Kazutaka Takahashi***, *Akihiko Ohtsu, Tomonori Takahashi, Aina Ushiyama, Motomasa Takahashi, Shuhei Yamaguchi, Masaki Morita, Takeshi Yoshioka, Nobuhiko Takano, Hiroshi Komatsu,* FUJIFILM Corporation, Japan

This study reports on the development of novel organosilicon precursors specifically tailored for the atomic layer deposition (ALD) process of silicon oxicarbide (SiOC) thin films. First, to design precursor structures effective for ALD, we established a computational framework for systematically evaluating the adsorption energy, activation energy, and reaction energy of precursors. This enabled the selection of an optimal precursor structure with a stable Si-C-Si backbone. Subsequently, we successfully synthesized the precursor based on a unique chemical path. The resulting ALD of the precursor demonstrated obviously higher growth per cycle (GPC) compared to conventional precursors, and the ALD film included Si-C-Si bonds well. Furthermore, by analyzing dependency of process temperature, precursor dose time, and ozone dose time, ALD based film growth mechanism was clarified. A notable challenge in high–temperature ALD processes is that the carbon concentration in the film generally decreases as process temperature increases. Moreover, process modifications aimed at increasing the carbon ratio typically led to a deterioration in both GPC and in–plane uniformity. In this work, however, by carefully optimizing the process conditions, we successfully achieved high carbon concentration,

high GPC, and good in–plane uniformity simultaneously, even under high–temperature deposition conditions.

AA-TuP-18 Modeling of Negative Capacitance FETs for Sub-60 mV/dec Switching through PEALD-HZO Ferroelectric Thin Films, ***Bo Hyeon Kim**, So Won Kim, Jae Hyuk Choi, Hee Chul Lee,* Department of Advanced Materials Engineering, Tech University of Korea

Since the discovery of negative capacitance (NC) in ferroelectrics, extensive research has been conducted in the field, with the Negative Capacitance Field-Effect Transistor (NC-FET) emerging as a breakthrough technology. NC-FETs have attracted significant attention for their ability to lower the subthreshold swing (SS) below the fundamental limit of 60 mV/dec at room temperature, making them highly advantageous for suppressing leakage current and realizing ultra-low-power devices.

In our previous study [1], we successfully deposited (HZO) ferroelectric thin films with relatively good polarization and reliability characteristics using a Co-Plasma ALD (CP-ALD) process, which simultaneously utilizes both direct and remote plasmas, as shown in Fig. 1. However, the inherent polarization hysteresis of ferroelectrics remains a significant challenge for switching device applications. To precisely control the NC characteristics, optimized capacitance matching through a ferroelectric-dielectric (FE/DE) stacked structure is essential [2].

Based on the characteristics of the HZO thin films deposited via our group's CP-ALD process, we modeled the electrical performance of MFIS-structured NC-FETs by stacking ferroelectric and dielectric layers, as illustrated in Fig. 2(a). For a 15-nm-thick ferroelectric HZO layer, the subthreshold swing (SS) was modeled as a function of the dielectric layer thickness, using Al_2O_3(k9) and HfO_2(k25) as the dielectric materials.

The results indicate that sub-60 mV/dec SS values are achieved when the dielectric thickness is below 1.4 nm for Al_2O_3 and 5.4 nm HfO_2. In particular, the most stable and lowest SS values were observed at thicknesses of 1.4 nm for Al_2O_3 and 3.8 nm for HfO_2. Especially, HfO_2 exhibited a much broader thickness window for maintaining an SS below 60 mV/dec compared to Al_2O_3. The optimized SS of the NC-FET improved by up to 12 mV/dec compared to that of a conventional MOSFET without a ferroelectric layer.

Additionally, to analyze the NC phenomenon in a practical polarization-switching environment, we will present modeling results based on the Nucleation-Limited Switching (NLS) theory, which accounts for the time-dependent transient polarization characteristics of ferroelectrics.

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AA-TuP-19 Enhancing Tetragonal Phase Stability of HfO_2 Dielectrics via Oxidation-State Engineering of VOx Interlayer, ***Yejin Han**, Woojin Jeon, Iksun Kwon,* Kyung Hee University, Republic of Korea*; Jaemin Kim, Duckhyeon Seo, Juhwan Jeong, Sunyoung Baik, Woongjin Choi, Kyuho Cho,* EGTM Co., Ltd., Republic of Korea

As Dynamic random-access memory (DRAM) capacitors continue to scale down, capacitance loss and increased leakage current become critical challenges, necessitating high-k dielectrics with improved phase stability. HfO_2 is widely used due to its high dielectric constant and adequate bandgap;[1] however, its stable monoclinic phase limits further equivalent oxide thickness (EOT) scaling, and stabilization of the tetragonal HfO_2 phase is therefore required.[2]

In this work, vanadium oxide (VO_x) was employed as an interfacial layer to modulate the interfacial oxygen environment and promote tetragonal HfO_2 formation. VO_x films were deposited by atomic layer deposition, and their oxidation states were analyzed by X-ray photoelectron spectroscopy as a function of process temperature. At 150 °C, the VO_x film exhibited a V^{5+}-dominant composition (84.22%, O:V = 2.88), whereas increasing the temperature to 300 °C increased the V^{4+} fraction to 58.07% (O:V = 2.16), indicating controllable oxidation-state tuning from V_2O_5-like to VO_2-like.

When an ultrathin VO_x interlayer (1–2 nm) was inserted between TiN and HfO_2, the tetragonal HfO_2 phase emerged after annealing, while no tetragonal phase was observed without VO_x. Post-annealing of VO_x at 500 °C revealed that VO_2(M) crystallization occurred only under an oxygen partial pressure of 25 mTorr, whereas higher oxygen partial pressures led to excessive oxidation and V_2O_5 formation.

In TiN/HfO_2/VO_x/TiN structures, the tetragonal HfO_2 fraction exhibited a dome-shaped dependence on oxygen partial pressure, reaching a maximum when the VO_x interlayer was VO_2-like (V^{4+}-dominant). These results demonstrate that oxidation-state-engineered VO_x effectively regulates interfacial oxygen vacancy conditions, enabling stable tetragonal HfO_2 formation and providing a viable pathway for advanced DRAM capacitor scaling. Such stabilization of the tetragonal HfO_2 phase is expected to enhance the effective dielectric constant, enable further EOT scaling, and improve leakage current characteristics through optimized oxygen vacancy control.

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AA-TuP-20 Minimisation of Platinum Loading on the Porous Transport Layer in Pem Water Electrolysers, ***Athina Tzavara-Roussi**, Volkert van Steijn, Ruud van Ommen,* Delft University of Technology, Netherlands

Proton exchange membrane water electrolysis (PEMWE) is considered a highly promising technology for converting intermittent renewable electricity into green hydrogen, yet it relies on scarce platinum-group metal for their catalytic activity and chemical stability, which could significantly limit scalability. The porous transport layer (PTL) is a critical component, typically made of titanium, on the anode of PEM electrolysers, since it facilitates the electron and mass transfer between the catalyst sites and the bipolar plates. A major challenge stems from the oxidation of the PTL in the highly oxidative anodic environment, which significantly reduces electrical conductivity and limits catalyst utilization. To protect the contact points between the anodic layers, the commercial solution involves the platinization of the PTL. However, this approach not only increases further the manufacturing costs, but also results in poor coating conformity thus risking its long-term durability.

This study investigates the use of ALD to achieve a conformal and uniform Pt coating on the PTL surface, in combination with evaporation to increase the coating thickness. We examine how the Pt loading, morphology, and thickness affect the performance and durability of the layer in a 4 cm^2 single PEM cell, identifying which coating configuration provides optimal protection for the PTL. Finally, we evaluate the deposition of iridium oxide to transform the PTL into a porous transport electrode and assess its electrochemical performance.

This project receives a Dutch National Growth Fund contribution from the programme NXTGEN HIGHTECH.

AA-TuP-21 Characterization of ALD-like SiCO Layers for MOL and BEOL Applications: Influence of Etching Plasma and Wet Clean, ***Alexandre Ponchon**, Emmanuel Petitprez, Pierre Brianceau, Benoit Martin, Melanie Dartois, Antoine Raison, Nicolas Gauthier,* CEA/LETI-University Grenoble Alpes, France

Atomic Layer Deposition (ALD) enables precise control of layer thickness at the atomic level, making it more suitable than Chemical Vapor Deposition (CVD) for etch stop layers (ESLs) in advanced transistor manufacturing. ESLs are crucial for precise pattern transfer and underlying structures protection during etching. As device dimensions continue to scale, there is an increasing demand for ultrathin and uniform ESLs with well-controlled thickness and etch selectivity.

In this work, we investigate the use of SiCO layers deposited by Single Precursor Activated Radicals Chemistry [1] (SPARC) process (a new technique in-between CVD and ALD), as SiN dry etch stop layer for MOL (middle of line) and BEOL (back-end of line) applications. We focus on the impact of the carbon elemental composition on the SiCO layer's resistance to standard wet clean chemistries and its ability to maintain ESL properties under etching plasma exposure.

We use 30nm thick SiCO layers, deposited at 400°C, with carbon content varying from 3% to 13%. We characterize the material resistance to standard wet clean chemistries and to two plasma etching chemistries (CH3F/O2/Ar and CH3F/H2), by monitoring the layer thickness before and after the process steps using a spectrometric ellipsometer. We assess the

impact of the etching plasma on the remaining SiCO material through Secondary Ion Mass Spectrometry (SIMS) elemental depth profiles.

Results show that SiCO layers exhibit high resistance to wet clean chemistries, with minimal thickness loss observed only in low carbon content films exposed to diluted HF, and its resistance increases as the carbon composition increases. After exposure to the plasma chemistries used for SiN dry etch, all SiCO layers show thickness reduction, with oxygen-based plasma causing greater removal than hydrogen-based plasma. Plasma etching modifies a few nanometers of the remaining SiCO film, which becomes an O-rich layer that can be removed with a dHF dip. The altered layer thickness is more substantial with hydrogen-based plasma, and higher carbon content results in shallower modifications.

These findings show that this SiCO layer deposited by SPARC is a promising material for MOL and BEOL ESL applications as it has a high resistance to both dry and wet etching processes while being easily removable after undergoing a plasma etch.

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AA-TuP-22 In Situ, Simultaneous Spectroscopic Ellipsometry and Quadrupole Mass Spectrometry Studies of Aluminum Doped ZnO Etching Using β-Diketones*, Maahir Rahi,* *Terrick Mcnealy-James, Justin Moore, Titel Jurca, Parag Banerjee,* University of Central Florida

Atomic layer etching (ALE) offers sub-nm level control over film removal and presents promising solutions to address patterning challenges in device manufacturing. These mechanisms become particularly important when the extended atomic structure of films such as crystal facets, grain boundaries, and dopants are taken into consideration.

In this work, we investigate the thermal ALE of aluminum doped zinc oxide (Al:ZnO) using β-diketonate-etchants such as, acetylacetonate (Hacac) and hexafluoro acetylacetonate (HFacac), by depositing monolayers of Aluminum into Zinc oxide. We utilize *in situ* spectroscopic ellipsometry (SE) and quadrupole mass spectrometry (QMS), enabling real time correlation between thickness evolution and reaction by-products. By coupling these techniques, this work provides insight into kinetics, reaction pathways, and the role of dopants.

AA-TuP-23 Terpineol Doped ALD Al_2O_3 Films for Low-K Materials: Effect of Terpineol Ratio and Metal Precursor Size on Structural and Dielectric Properties*, Sovendo Talapatra,* *Noah Zahn, Nicholas Strandwitz,* Lehigh University

Research on low-κ dielectric materials is becoming critically important to deal with capacitance delays of due to decreasing dimensions of integrated circuits. Herein, we will report the structural and dielectric properties of terpineol-doped Al_2O_3 films where terpineol acts as a sacrificial agent or porogen, leaving porosity in the films after post-deposition annealing treatment. Terpineol-doped films were deposited by atomic layer deposition (ALD) and the modification of the porosity by changing the ratio of terpineol pulse in between the metal precursor and H_2O co-reactant was explored. The choice of metal precursor also influences the porosity generation in the film because of the steric hindrance and reactivity of the precursor. Three metal precursors, trimethylaluminum (TMA), aluminum tri-sec-butoxide, and tri-i-butylaluminum will be used to study the density, dielectric constant of the films. X-ray reflectivity will be used to measure the density of the films. For TMA to terpineol ratio 1:1, initial result showed 17% decrease of density for as deposited terpineol doped films than ALD Al_2O_3 at 120°C. Dielectric constant of the films will be measured using capacitance-voltage measurement. For as-grown terpineol-doped films the initial measurement also showed dielectric constants as low as 4 compared to a value of ~7 for ALD grown Al_2O_3. Our work shows that small molecule inclusions in ALD is a useful strategy for the growth of porous and low-κ thin films, while still retaining the benefits of precise thickness control and conformality afforded by ALD.

AA-TuP-24 High Rate, Tuneable Dielectric Nitrides by Plasma Atomic Layer Deposition Enabling Volume Manufacturing for Gan Device Integration*, Arpita Saha,* *Elliot Gay, Dmytro Besprozvannyy, Aileen O'Mahony, Michael Powell, Andrew Newton,* Oxford Instruments Plasma Technology, UK

Gallium Nitride (GaN) has recently expanded into power electronics, RF,microLEDs and VCSELsmarkets.The adoption of GaN transistors in high volume consumer-based power electronicsis driven by the need for smaller, faster, efficient mobile device chargers.It has been predicted the GaN power device market will reach $3B by 2030[1]supported by a broader range of applications including renewable energy, data centres, electric vehicles, and infrastructure for 5G and 6G networks.

These emerging GaNmarkets require uniform,conformal,low damage plasma processing solutions optimised for 200 mm wafers to improve device performance,throughput, andyieldat reduced cost.Plasma enhanced atomic layer deposition (PEALD) has been used in GaN transistors for low damage,[2]uniform passivation layers (Al_2O_3,[3] SiN), as a method of optimizing the interface using native oxide removal nitridation[4,5]followed by deposition of high-quality nitrides like AlN.

High throughput plasma ALD of SiN is beneficial for GaN device processing at low temperature (≤500 °C) compared to LPCVD (≥700 °C)and thermal ALD (>450 °C) without compromising on conformality (compared to PECVD)[10]or uniformity up to 200 mm wafer size. PEALD SiN has also been shown to reduce trap defect density in GaN transistors compared to other deposition techniques and materials.[11]Optimisation of the plasma processing parameter scan achieve SiN films with tuneable growth rate,composition,and refractive index.[12, 13].

PEALD processes forAlN and SiN have been developed achieving excellent thickness and refractive index uniformity across 200 mmSi wafers using Oxford Instruments Atomfab ALD system which uses apatented capacitively coupled (CCP)[3] remote plasma source. Using Oxford Instruments' novel CCP remote plasma source, and a low chamber volume, increase in deposition rate has been achieved when comparing to an inductively coupled plasma source (ICP) process. For example, we have been able to achieve 8 times faster deposition rate for AlN films using our CCP remote plasma source compared to ICP plasma.The composition of the AlN and SiN films were measured by XPS resulting in low C% and O% content. The ToF-ERDA showed low H% content in SiNx films while the wet-etch rate was better for the films produced using the CCP plasma source compared to the films produced by ICP plasma source. The breakdown voltage and the dielectric constant for the as deposited SiNx film obtained was >10.5 MV/cm and >6 for 30 nm film respectively.

To support the production ramp of the GaN transistors, high throughput tuneable AlN and SiN processes using plasma ALD along with optimized surface pre-treatment has been developed by Oxford Instruments negating the need for extended plasma exposure,high temperature depositionor temperature ramping within the process.The estimative wafers produced per hour for AlN (3 nm films) is 11 WPH and for SiNx (5 nm films) is 10 WPH.

AA-TuP-25 Enhanced Electrical Characteristics in CAAC-IGZO Memory Devices Using 2600W Remote-Plasma-Processed HfO_2 and H_2 Passivation at the CAAC-IGZO/Al_2O_3 Tunneling Interface*, Hyeon Wu Nam,* *Chang Bun Yoon, Byung Wook Kim, Yong Woon Jang, Min Kyun Kang, Chang Yun Hong,* Department of Advanced Material Engineering, Tech University of Korea

Charge trap memory devices employing a sputtered CAAC IGZO channel were fabricated using an $Al_2O_3/HfO_2/Al_2O_3$ dielectric stack as the blocking, charge trapping, and tunneling layers. All dielectric layers were deposited by remote plasma atomic layer deposition, while the CAAC IGZO channel was formed by sputtering to preserve its crystalline–amorphous composite structure. The electrical characteristics of the devices were systematically compared with those incorporating dielectric layers deposited by direct plasma ALD. Devices with remote plasma–processed dielectrics exhibited an enlarged memory window and reduced leakage current. Material analysis revealed a decreased concentration of oxygen vacancies in the HfO_2 charge trap layer for the remote plasma ALD process compared to direct plasma ALD. In addition, remote hydrogen plasma treatment was employed at the channel–tunneling layer interface, effectively passivating interfacial defects between the CAAC IGZO channel and the Al_2O_3 tunneling layer. This interfacial defect reduction enhanced charge injection and trapping efficiency. The combined effects of reduced bulk defects in HfO_2 and improved interfacial quality in the dielectric stack contribute to enhanced charge storage characteristics in CAAC IGZO–based memory

devices.

Quantitatively, the incorporation of remote plasma–processed dielectrics led to a substantial enhancement in device performance, with the memory window expanded by up to ~6 V, a ~0.1 V dec^{-1} improvement in subthreshold swing, and an on/off current ratio increased to the order of $\sim10^7$.In addition, the field-effect mobility reached values as high as ~20 $cm^2 V^{-1} s^{-1}$, demonstrating that the RP approach effectively improves both charge storage capability and channel transport characteristics.

This work was supported by K-CHIPS(Korea Collaborative & High-tech Initiative for Prospective Semiconductor Research) (2410011219, RS-2023-00237030, 23027-15FC) and by the Technology Innovation Program (Materials & Components Technology Development (R&D)– Package-type) (RS-2025-02220734, Development of Manufacturing Technology for High-Purity iron chloride (>99.5%) and Sodium Silicate (>97.0%) via Utilization of Bayer Process Byproducts) funded By the Ministry of Trade Industry & Energy(MOTIE, Korea).

AA-TuP-26 Impact of Oxidant on Conformal HZO ALD in High Aspect Ratio Structures, ***Soham Shirodkar**, Dushyant Narayan,* The University of Texas at Dallas*; Dan N. Le,* RASIRC, University of Texas at Dallas*; Thi Thu Huong Chu, Soubhik De, Minjong Lee,* The University of Texas at Dallas*; Adrian Alvarez, Lorenzo Diaz,* RASIRC*; Jiyoung Kim,* The University of Texas at Dallas

The scaling of advanced DRAM technologies requires complex structures with high aspect ratio (HAR) trenches and cavities and is currently transitioning to 3D integration to sustain performance improvements.[1] Hafnium based oxides are key materials for the cell capacitor in DRAM cells due to their high dielectric constant and wide bandgap. To achieve conformal growth in HAR structures, ALD processes often use large precursor and oxidant doses to ensure reactant transport into deep features [2]. However, excessive oxidant dosing can promote undesirable interfacial oxidation, particularly on metal electrodes. To address this, we identify differences in oxidant efficiency during HAR filling and evaluate the role of various counter-reactants on conformal growth.

To understand the effect of counter reactant choice, we first investigated growth characteristics on planar substrates. We found that the oxidant dose required to reach saturation was different for each oxidant. Namely, we found that H_2O_2 required a smaller dose than O_3 to saturate each ALD cycle. Saturation at a reduced oxidant dose implies a potential for improved filling in HAR structures at lower doses while mitigating excessive interfacial oxidation due to high dosing.

Based on the observations for planar substrates, vertical HAR substrates with AR ranging from ~20:1 up to ~60:1 were used to evaluate the conformality of each process. Furthermore, to enable quantification of penetration depth, specially designed horizontal Ultra-HAR structures with AR up to 10,000:1 were used, and analysis of growth areas were performed using SEM and EDX (Fig. 1). The extent of growth into the cavity was used to assess the deepest achievable filling as a function of both oxidant and precursor dosing. Alongside the horizontal structures, conformality was also evaluated in vertical trenches with smaller critical dimensions, providing access to more extreme confinement where precursor transport is further limited (Fig. 2). We found that increasing precursor dose improves transport into confined geometries, with signatures of oxidant-dependent effects on HAR filling. Overall, these results show that oxidant choice plays an important role in ALD growth in HAR structures for the stringent demands of next-gen semiconductor devices.

We acknowledge RASIRC for providing BRUTE® Peroxide and TMEIC for providing the ozone generator (OP-250H). This work was supported by Samsung Electronics Co., Ltd. (No. IO221018-03002-01). We would also express our gratitude to Chipmetrics for providing the UHAR substrates.

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AA-TuP-27 Stable High-k Morphotropic Phase of $HfZrO_4$ Using Uniformly Distributed Dopants, ***Nguyen Vu**, Charlene Chen, Sunil Ghimire, Ray Meck, Jared McWilliams,* EMD Electronics, USA

Since the 1950s, the morphotropic phase boundary (MPB) has attracted considerable attention due to the anomalous increase in the dielectric constant in this region. It is now gaining rapid growth in research on hafnia-based dielectrics as a novel approach to achieve low equivalent oxide thickness (EOT) without sacrificing leakage. Unlike the traditional nanolaminate approach, this work investigates the formation of the MPB phase in HZO dielectrics with uniformly distributed dopants through atomic layer deposition and annealing within the back-end-of-line thermal budget. It is found that the more homogeneous the dopant distribution, the better the dielectric performance. The resulting doped HZO with a physical thickness of 50 Å exhibits a low leakage current of $2x10^{-5}$ A/cm^2 and an EOT of 5.4 Å. Different strategies for achieving the desired dopant distributions are discussed, highlighting the potential of precursor development to reach the optimal performance.

AA-TuP-28 ALD Oxide Coatings for Anti-Stiction MEMS Applications Compatible with 500 and 1000 °C Wafer Bonding, ***Eric Reed**, Matthew Weimer, Arrelaine Dameron,* Forge Nano*; Robert MacDonald, David Lin,* GE Aviation, USA*; Mohammad Megdadi,* University of Nebraska - Lincoln*; Mary Ann Maher,* Soft MEMS

As MEMS devices continue to shrink and the operational range demands increase, they increasingly suffer from irreversible stiction, in which surface forces, such as van der Wall forces and electrostatic forces, exceed the forces required to separate moving components, the restoring force. Some attempts to reduce surface adhesion include the reduction of surface energy by application of self-assembled monolayers (SAM) or diamond-like carbon coatings (DLC) and low surface area contact points, such as bump stops. However, these methods become less effective as MEMS devices continue to approach nanoscales. For example, SAM coatings become more susceptible to defects and non-conformal films as the aspect ratio increases. Additionally, DLC and SAM coatings are incompatible with high-fidelity packaging methods, like direct wafer bonding, which occurs under >1000 °C annealing conditions. DLCs suffer from adhesion instability while SAM coatings completely degrade at this temperature. Atomic Layer Deposition (ALD) overcomes these deficiencies by providing conformal, temperature-stable films. Engineering surface roughness and film stability is, therefore, one path to improving device reliability. This study investigates which ALD thin films provide the greatest surface roughness with sufficient adhesion to silicon substrates. Silica (SiO2), hafnia (HfO2), and titania (TiO2) films were deposited on Si 〈100〉 coupons using thermal ALD and subsequently annealed in an inert environment, at 500 °C and 1000 °C, to simulate various MEMS wafer bonding processes. The films were evaluated for changes in crystallinity, surface roughness, and composition. SiO2, used as a control, exhibited minimal changes in structure and roughness. HfO2, initially polycrystalline, showed increased crystallinity and surface roughness with annealing while maintaining film stability. When applied to a MEMS test structure, the 1000 °C annealed HfO2 film showed a significant reduction in stiction, compared to the coated features. In contrast, TiO2 underwent a significant crystallographic phase transition at >700 °C and delaminated, likely due to film stress. These results indicate that polycrystalline HfO2 offers a stable, roughened surface capable of reducing attractive forces responsible for MEMS stiction failures. Future work will evaluate thermally deposited ALD HfO2 directly on MEMS accelerometers and gyroscopes to quantify its impact on device performance and reliability.

AA-TuP-29 Enhancing ZrO_2–based DRAM capacitor performance by employing atomic layer deposited In_2O_3 electrode via Mo doping, ***Hunseok Son**, Woojin Jeon,* Kyung Hee University, Republic of Korea

As dynamic random-access memory (DRAM) scales down to achieve higher integration, electrode engineering to mitigate insufficient capacitance and excessive leakage current remains a critical challenge. TiN electrodes and ZrO_2 dielectrics are widely used in metal-insulator-metal (MIM) capacitors because of their excellent process compatibility. However, TiN electrodes deplete oxygen from ZrO_2 at the ZrO_2/TiN interface via an oxygen-scavenging effect, forming undesirable TiO_xN_y. This accelerates leakage and degrades performance.[1] The formation of these oxygen defects degrades not only the electrical characteristics but also the overall performance of the MIM capacitor. The initial spacing is not correctly formatted. Furthermore, nitrogen diffusion into ZrO_2 reduces the bandgap, resulting in degradation of leakage current characteristics.[2] Therefore, oxide-based electrodes are more suitable for use with ZrO_2 than nitrogen-based electrodes. To overcome these limitations, we propose an approach that uses Mo-doped In_2O_3 bottom electrode grown by atomic layer deposition (ALD). During thermal treatment, Mo-doped In_2O_3 exhibits a change in oxidation state to Mo^{4+}, which substitutes for In^{3+}, resulting in high electrical conductivity due to increased free electrons and low resistivity. [3] Furthermore, its low roughness provides excellent electrode characteristics for MIM capacitors. [4] In terms of crystallinity, here to, the initial spacing is incorrect. The cubic phase In_2O_3 (400), formed by Mo doping in In_2O_3, exhibits good crystallographic compatibility with the tetragonal phase ZrO_2 (002). The formation of t-ZrO_2 (002) enables higher

capacitance in ZrO_2-based MIM capacitors fabricated on Mo-doped In_2O_3. The high work function (~5 eV[5]) of Mo-doped In_2O_3 provides a distinct advantage over TiN (~4.2 eV[6]). This high work function contributes to leakage suppression, thereby enhancing the device's overall performance. Additionally, In_2O_3 has a significantly lower oxygen vacancy formation energy (~2.4 eV) than ZrO_2(~6.2 eV), enabling oxygen transfer to ZrO_2.[5] This mechanism not only suppresses the formation of sub-interface oxides, unlike TiN electrodes, but also reduces defect density within the ZrO_2 layer, minimizing unwanted conduction and improving interface stability. Consequently, replacing TiN with the ALD-grown Mo-doped In_2O_3 bottom electrode offers a practical, scalable solution. Mo-doped In_2O_3 provides sufficient capacitance while suppressing leakage current and enhancing stability, thereby strengthening the integrity of the MIM capacitor structure. This paves the way for continued dielectric scaling and improved reliability in advanced DRAM technology.

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AA-TuP-30 Advanced Seamless Lateral Gap-fill Process for 3D Structures via a New Approach, ***Yudeuk Kim***, *Seunghee Cho, Kwangseon Jin,* Wonik IPS, Republic of Korea*; Hoon Kim,* Wonik IPS*; Wontae Noh, Taewan Lee, KYUNGPIL NA, Jaehun Lee, Jiwon Moon, Hyung mook Lim,* Wonik IPS, Republic of Korea

Like 3D NAND scaling progresses, the integration of 3D DRAM and advanced logic architectures requires highly conformal dielectric gap–fill capability within increasingly complex high–aspect–ratio structures. Conventional deposition schemes optimized for vertical profiles exhibit insufficient step coverage in lateral cavities, resulting in seam and void formation due to precursor transport limitations and restricted surface reaction accessibility. Moreover, the enlarged effective surface area significantly reduces throughput, forcing reliance on iterative deposition–etchback cycles that remain inefficient and inherently unsuitable for uniform lateral gap–fill.

To overcome these limitations, a novel ALD based gapfill strategy has been developed, enabling fully seamless void free filling across both vertical and lateral geometries. TEM analysis confirms that while conventional processes show pronounced internal seams shown in Fig. 1 (a), the newly engineered process demonstrates complete elimination of interfacial defects, ensuring structurally dense and continuous films throughout the entire 3D topology in Fig. 1 (b). This approach delivers improved structural robustness, enhanced conformality, and high productivity, positioning it as a key enabling technology for next generation high density 3D device fabrication.

AA-TuP-31 ***Modeling the Dynamics of Surface Coverage in Atomic Layer Deposition for Multilayer Lateral Trench Structures*****, *Jin Hak Kim***, *Yoon Jae Won, Jun Soo Shin,* WONIK IPS, Republic of Korea

As AI technology advances and the need for high-performance memory semiconductors increases, 3D DRAM manufacturing technology is one of the promising technology to increase memory capacity. To reduce high experimental costs and increase process development speed, it is important to estimate processing time in the atomic layer deposition process. As the number of lateral trenches increases, the adsorption area increases compared to when there are only vertical trenches. Our simulation shows that the minimum saturation time for conformal atomic layer deposition is proportional to the aspect ratio in the lateral and vertical directions. Due to the effect of gas particles being re-emitted from the bottom of the trench, the minimum surface coverage area is located away from the bottom of the lateral and vertical trench surfaces. The result is similar to those in a paper simulating adsorption inside lateral channels.1

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AA-TuP-32 Nucleation Dependence of ALD on Diamond for Surface Processing in Quantum Applications, ***Jessica Jones***, *Jeffrey Elam,* Argonne National Laboratory, USA

The surface termination and interfacial interactions of materials for quantum technologies are critical.Use of atomic layer deposition (ALD) has been explored to provide insight on the chemical environment of the surface while passivating the surface.We explore the nucleation and growth of ALD Al_2O_3 and TiO_2 on diamond surfaces used for quantum sensing.We demonstrate the suppression of dark spins on diamond surface after coalescence of the TiO_2 ALD film on the surface.Additionally, we demonstrate that the nucleation of ALD Al_2O_3 using dimethylaluminum isopropoxide (DMAI) and water is sensitive enough to distinguish between the common surface termination types (H- terminated and O-terminated).We also evaluated methods to pretreat the diamond surface prior to passivating the surface with ALD Al_2O_3. We used in situ spectroscopic ellipsometry measurements to monitor the surface reactions and evaluate the ALD Al_2O_3 nucleation process as a function of different ex situ and in situ surface pretreatments. We found that in situ water dosing and high vacuum annealing provided the most favorable environments for nucleation of ALD Al_2O_3 using DMAI and water ALD. Hydrogen termination passivated both smooth and rough surfaces while triacid cleaning passivated the smooth surface only, with striking effectiveness.

AA-TuP-33 Atomic Layer Deposition on Reduced Activation Ferritic Martensitic Steel for Nuclear Fusion Applications, ***Soren Bentley***, UK Atomic Energy Authority, UK*; Zachary Robinson, Mark Wittman,* University of Rochester*; Matthew Sharpe,* University of Rochester, UK*; Rashad Ahmadov, Josh Ruby,* University of Rochester*; Jeffrey Woodward,* Naval Research Laboratory*; Alexander Kozen,* University of Vermont

Nuclear fusion holds immense potential to reshape the global energy landscape. To develop mature technologies that can be deployed at power-plant scale, numerous materials-science challenges must be solved. One critical example is the safe, efficient, and loss-free handling of tritium (hydrogen-3), an essential fuel for fusion energy. Tritium permeates many of the materials used in reactor components, leading to structural embrittlement and other hazards associated with the fuel's radioactive properties. Atomic layer deposition (ALD) is emerging as a promising technique for the development of Al_2O_3 permeation barrier coatings that reduce loss of tritium. ALD's ability to produce high-quality, uniform films across complex geometries and components makes it advantageous compared to techniques limited to planar substrates. Though ALD Al_2O_3 coatings are well studied on semiconductor-relevant substrates, the work presented here reports the use of a custom-built ALD system to carry out the first syntheses on fusion-grade reduced-activation-ferritic-martensitic (RAFM) steel.

Prior to deposition, 1 cm × 1 cm RAFM steel substrates were prepared by polishing them to ~15 nm root mean square surface roughness. Al_2O_3 films were then deposited using a thermal ALD process with trimethylaluminum (TMA) and water precursors. Deposition was performed at temperatures between 100–200 °C to determine optimal growth conditions. Once this was achieved, growth rate curves were measured.

The films were characterized using X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), X-ray reflectivity (XRR), and spectroscopic ellipsometry. Our XPS results indicate that the RAFM surface is predominantly iron, in addition to small quantities of chromium oxide. ALD films were primarily stoichiometric Al_2O_3, with some growth conditions resulting in a small aluminum hydroxide component. The XRR and ellipsometry data were used to determine film characteristics such as morphology and ALD film thickness. This required the development of a model in which the film was represented as three layers: a low-density surface oxide, a denser bulk oxide, and an interface oxide in contact with the substrate surface. Growth rate curves and other process development will be presented.

AA-TuP-34 Mitigating Bow CD in Sub–20 nm HARC: SEM3D Modeling of Mask Taper and Cyclical Deposition–Etch Dynamics, ***Prabhat Kumar***, *Lin Yu, Lin Zhao, Harsh Meena, Min Huang, Nandita Ghodki, Sankar Sarma, Sasan Shadpour, Jeff Lucas, Mingmei Wang, Taner Ozel,* Lam Research Corporation

As HARC feature sizes push below 20nm, maintaining stringent critical dimension (CD) control is essential for device performance, reliability, and yield. In advanced etch stacks, post–etch profiles are highly sensitive to incoming mask geometry, with across–wafer bow CD emerging as a dominant systematic variation. Tapered or necked mask profiles exacerbate ion angular scattering and polymer transport imbalance, producing non–uniform sidewall evolution and CD drift. To quantify and mitigate these effects, we employed a physics–based SEMulator3D (SEM3D)† workflow calibrated via Bayesian optimization to experimental profiles and plasma fundamentals. The calibrated model captured ion–limited etching, neutral–assisted deposition, and polymer redeposition, with the incident ion angular distribution represented by a Voigt profile consistent with pulsed–bias operation.

Tapered, straight, and reverse taper masks revealed a near linear dependence of both bow CD and mask selectivity on mask taper: larger taper increases bow while improving selectivity due to a larger effective

opening. A design of experiments (DOE) varying top and bottom CDs confirmed the trade space—bow CD decreases with smaller bottom CD, whereas selectivity improves with larger top CD—exposing a fundamental limitation when taper is left unaddressed. To break this constraint, we introduced a targeted deposition step engineered to reduce taper and drive the mask toward a straighter geometry prior to etch. By tuning the sticking coefficient of depositing neutrals, we modulated within via deposition depth—lower sticking promoted deeper, more conformal coverage—thereby straightening the sidewall and suppressing taper induced aberrations. Simulations showed substantial bow reduction for straightened profiles.

In addition, we investigated **cyclical deposition–etch** sequencing to manage the *dynamic* evolution of bow and the risk of top–CD clogging. A dedicated cyclical–process DOE varying sticking coefficient, per–cycle deposition thickness, and cycle count demonstrated that bow growth rate can be actively controlled by tuning deposition parameters and cadence. Low–sticking, moderate–thickness cycles provided the best balance—minimizing bow growth (30–60% retardation observed in simulation) while avoiding opening pinch–off—whereas high–sticking films favored top–side accumulation and premature constriction.

Overall, this study quantifies its impact with a calibrated SEM3D model and demonstrates two complementary mitigation paths: (1) pre–etch deposition to straighten the incoming profile and (2) optimized cyclical deposition–etch to dynamically stabilize sidewalls and suppress bow growth without inducing clogging. Together, these strategies improve across–wafer CD uniformity and expand process window for next–generation HARC nodes.

†SEMulator3D® is a semiconductor process modeling platform that offers wide ranging technology development capabilities. This product is offered through Lam Research.

AA-TuP-35 Low-Temperature ALD Rutile TiO_2 Buffer Layers for VO_2-Based Smart Windows: Towards Flexible Substrates, ***Jan Leithäuser***, *Waafa Al Nachwati, Philip Klement, Jörg Schörmann, Sangam Chatterjee, Martin Becker,* Justus Liebig University Giessen, Germany

Vanadium dioxide (VO_2) is a premier candidate for thermochromic smart windows due to its ability to dynamically modulate solar heat gain. However, achieving high solar modulation (ΔT_{sol}) typically requires a rutile-phase TiO_2 buffer layer to lower the growth temperature of VO_2 [1]. Such buffers are often produced via high-temperature sputtering (>400 °C), limiting the use of temperature-sensitive flexible substrates.

In this work, we demonstrate a low-T ALD route to rutile TiO_2 at process temperatures as low as 220 °C. Utilizing a thermal TDMAT/H_2O process at 200 °C [2,3], we generate "black TiO_2" films. Based on literature [2,3], the characteristic Ti^{3+} defects and oxygen vacancies in these films are believed to bypass the common high-temperature anatase-rutile conversion.

Integrated into $VO_2|TiO_2|$glass architectures, we achieve ΔT_{so} > 9% comparable to benchmarks using high-temperature sputtered references (650 °C) [1]. Crucially, this approach removes a major barrier for VO_2 coatings on polymer-based substrates. Preliminary results indicate that this low-T process can be transferred to polyimide (PI), paving the way for flexible VO_2 smart windows.

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AA-TuP-36 ALD and Surface Chemistry of p-type Tin Oxides, *Asare Dua, Michael Foody,* Illinois Institute of Technology*; Bo Liu,* ***Adam Hock***, illinois Institute of Technology

Low temperature ALD of p-type conducting oxides remains a challenge, particularly as surface chemistry can dominate contact quality and therefore device performance as a function of overall scaling.Furthermore, the surface of p-type oxides is often susceptible to reaction with atmospheric oxygen and water, altering dopant concentrations and affecting process conditions.We have developed a new tin ALD precursor and utilized it for low-temperature, thermal ALD of p-type tin oxides.We have characterized the chemical and physical properties of the precursor, its ALD growth window, and resulting p-type film mobilities.We also have studied the effects of surface treatments on mobility and stability of the resulting films.

In this talk we discuss the results of these studies on p-type tin oxide thin films grown using a novel precursor.This includes QCM measurements under ALD conditions, solution model reactions, and synchrotron studies conducted at the Advanced Photon Source (APS) located at Argonne National Laboratory.The surface reactions of Sn precursors and half-reactions provide insight into the surface of the film and overall manufacturability of p-type oxides in the future.The results of these studies were applied to improved p-type oxide ALD, including doping strategies.Device characterization will also be discussed as time allows.

Area Selective ALD
Room Tampa Bay Salons 5-9 - Session AS-TuP
Area Selective ALD Poster Session

AS-TuP-1 Modifying Polymer Inhibitors for Enhanced Selectivity in Area-Selective ALD of Al_2O_3 on Silicon, ***Amnon Rothman***, *Renana Didi,* Ben Gurion University Be'er Sheva, Israel

Area-selective atomic layer deposition (AS-ALD) via area-deactivation using polymer inhibitors has emerged as a promising approach for achieving directional thin film growth without photolithography. While polystyrene (PS) has demonstrated effectiveness as a blocking agent, optimizing its chemical properties remains an underexplored avenue to enhance selectivity, particularly for ultra-thin film applications. This work investigates the impact of polymer structure modification on AS-ALD selectivity, specifically examining the use of fluorine-terminated polystyrene (PS-F) as an inhibitor for selective Al_2O_3 deposition on silicon substrates with native oxide.

The hypothesis underlying this study is that fluorine functionalization of polystyrene will provide superior blocking characteristics compared to unmodified polystyrene, enabling enhanced selectivity at reduced polymer film thicknesses. Both pristine polystyrene and fluoro-polystyrene were deposited onto silicon substrates via spin-coating, yielding distinct thickness profiles that were characterized through spectroscopic ellipsometry.

Subsequent to polymer deposition, selective Al_2O_3 ALD was performed using trimethylaluminum (TMA) and water as precursors. The selectivity was evaluated using complementary *ex-situ* characterization techniques: ellipsometry for film thickness measurement on both inhibitor-covered and unprotected regions, and X-ray photoelectron spectroscopy (XPS) for depth profiling and chemical composition analysis to confirm selective deposition and polymer decomposition behavior.

Preliminary aspects of this investigation also explore selective growth on patterned architectures, including potential applications on metallic (copper) surfaces, to assess the generalizability of the polymer-inhibitor approach across diverse substrate compositions. This work aims to establish structure-function relationships between polymer inhibitor design and AS-ALD selectivity, providing guidelines for rational optimization of blocking agents in selective film synthesis.

AS-TuP-2 Probing the Effects of Reaction Byproducts on Atomic Layer Deposition Selectivity, *Jessica Jones, Cong Liu,* ***Alex Martinson***, Argonne National Laboratory

Reaction byproducts produced during ALD result in unintentional and variable exposure to small molecules, which may alter the site-specific mechanistic pathways for ALD nucleation. We observe that the wide variability in the nucleation density of ALD Al_2O_3 (with dimethylaluminum isopropoxide and water) on oxidized TiO_2(110) single crystals is reduced by intentional pretreatment with one of the reaction byproducts - isopropyl alcohol (IPA). The first cycle of ALD growth is observed to be an early and strong indicator of the ALD nucleation density, substantiating previously reported nucleation models that rely upon this largely untested assumption. Rapid and nondestructive small molecule pretreatments, including IPA and water, are also observed to be a probe of surface defects, including TiO_2(110) oxygen vacancies, that are correlated with site-selective ALD nucleation. The nonidealities associated with reaction byproduct production during ALD inspire novel surface pretreatment methods that improve reproducibility and may serve to more efficiently probe defects/minority sites surfaces. A detailed mechanistic understanding and control of site-selective ALD processes require consideration of reactivity for both chemical precursors and reaction byproducts.

AS-TuP-3 Inhibitor Selection for Area-Selective SiO Deposition: Limited Growth on SiO Surfaces and Unrestricted Growth on SiN Surfaces through Theoretical and Experimental Studies, ***Tomoya Nagahashi***, *Kimihiko Nakatani, Takayuki Waseda, Shoma Miyata, Keitaro Hamada, Nozomu Takano, Hajime Karasawa, Ryota Horiike, Yoshitomo Hashimoto, Yoshiro Hirose,* KOKUSAI ELECTRIC CORPORATION, Japan

Silicon oxide (SiO) is a crucial insulator material for semiconductor devices, and area-selective deposition of SiO thin film on silicon nitride (SiN) surfaces, while avoiding deposition on SiO surfaces, is essential for further device scaling in logic, DRAM, and NAND applications. Area-selective deposition can be realized using inhibitors that adsorb on surfaces where deposition is undesired. Hydroxyl groups (–OH) on SiO surfaces serve as chemisorption sites for these inhibitors. In this study, we selected potential inhibitors from various molecules, including aminosilanes and halogenated silanes, through first-principles calculations to achieve higher selectivity, followed by experimental evaluation of the selected inhibitors.

Our theoretical approach focused on three key factors: chemisorption reactivity, by-product effects, and inhibitor size. For chemisorption reactivity, lower activation energy (Ea) and negative Gibbs free energy of formation (ΔG) for inhibitor adsorption onto –OH sites contribute to increased reactivity, leading to higher inhibitor coverage. The inhibitor chemisorption generates by-products, and their physisorption competes with inhibitor chemisorption, reducing inhibitor coverage; thus, preventing by-product physisorption is critical. Regarding inhibitor size, smaller molecules enable higher surface density on SiO surfaces, potentially enhancing inhibitor performance.

ΔG calculations indicated that by-product physisorption does not occur for any candidate inhibitors. We identified three highly reactive aminosilanes with the structure $(R_A)_3Si–N(R_B)_2$, where R_A is identical and R_B varies, influencing size. To assess the influence of molecular size on selectivity, we chose the largest and smallest inhibitors from these aminosilanes, AS_L and AS_S, for experimental evaluation. Chemisorption of AS_L and AS_S on SiO and SiN surfaces was analyzed using static secondary-ion mass spectrometry (static-SIMS). The static-SIMS analysis detected signals corresponding to the chemisorbed inhibitor structure $–Si(R_A)_3$ after gas exposure, with AS_S exhibiting greater coverage on SiO surfaces compared to AS_L. Both inhibitors exhibited preferential adsorption on SiO over SiN, improving selective deposition. Furthermore, SiO film deposition via atomic layer deposition (ALD) using AS_L as an inhibitor demonstrated significantly reduced growth on SiO surface compared to SiN surface, achieving far greater selectivity than without inhibitors. We anticipate even higher selectivity by employing AS_S and optimizing process conditions. Our combined theoretical and experimental findings pave the way for advanced area-selective deposition and continued device scaling.

AS-TuP-4 Inverse-Gradient Atomic Layer Deposition in High-Aspect-Ratio Structures Using Physical Interaction of a Removable Small Molecule Inhibitor, ***Jiwoo Oh***, *Woohyuk Kim, Woo-Hee Kim,* Hanyang University, Republic of Korea

We report a topographically selective atomic layer deposition (ALD) strategy based on depth-dependent growth suppression that enables inverse-gradient growth of HfO_2 thin films in high-aspect-ratio (HAR) structures, in which the step coverage progressively increases from the top toward the bottom of the feature. This growth behavior is realized through an ABC-type supercycle ALD scheme incorporating a vapor-dosed surface protector (SP) that preferentially adsorbs on the more accessible top surfaces and upper sidewalls, thereby selectively suppressing film growth in these regions while enabling relatively enhanced deposition in the lower portions of HAR structures. X-ray photoelectron spectroscopy (XPS) analysis confirms the absence of residual carbon- or nitrogen-related impurities, indicating that the SP does not perturb the intrinsic film chemistry. The resulting HfO_2 films exhibit film density and electrical performance comparable to those of reference ALD films, including dielectric constant, leakage current density, and breakdown strength. Cross-sectional transmission electron microscopy (TEM) analysis further reveals a monotonic increase in film thickness along the trench depth, directly demonstrating effective inverse-gradient growth behavior. Overall, this strategy provides a practical route for conformality control in HAR structures under high-temperature ALD conditions, offering a viable process approach for advanced three-dimensional memory device fabrication.

AS-TuP-5 Perfluoroalkylpolyether Thin Layer–Induced Inhibition of Al_2O_3 Atomic Layer Deposition with a Trimethylaluminum Precursor, *Hiroaki Iwamoto,* ***Yuki Shibutani,*** AGC Inc., Japan

Area-selective atomic layer deposition (AS-ALD) is a promising approach for next-generation semiconductor device fabrication because it can reduce or eliminate conventional steps such as photolithography and etching when forming complex patterns.[1] To realize this, many studies have focused on enhancing selectivity through surface pretreatments or by modifying ALD processes, for example by introducing deposition/etch cycles.[2] One effective strategy is the use of inhibitor molecules that passivate non-growth regions toward ALD precursors and reactants. However, the size and chemical reactivity of the ALD precursors strongly affect the inhibitory performance of these molecules. As a result, highly selective AS-ALD has often relied on bulky, less reactive precursors, which typically exhibit low growth per cycle (GPC).[3] Although surface treatments by fluorinated molecules are known to reduce surface energy and suppress physisorption of various species, perfluoroalkyl-functionalized surfaces have shown only limited inhibition capability in Al_2O_3 ALD when trimethylaluminum (TMA)—a very small and highly reactive precursor—is used.[4]

In this study, we investigate a perfluoroalkylpolyether (PFPE)-substituted trialkoxysilane (inhibitor **1**) as an inhibitor that enables efficient suppression of Al_2O_3 growth in TMA-based ALD. PFPE possesses a highly flexible fluorinated backbone; unlike perfluoroalkanes, the ether oxygens reduce steric congestion and facilitate molecular mobility. The inhibitor monolayer was formed by coating the compound onto UV/O_3-treated Si substrates, followed by thermal treatment. Al_2O_3 ALD was then performed using TMA and H_2O at a substrate temperature of 200 °C, with a GPC of 0.7 Å. Inhibition performance was quantified by X-ray photoelectron spectroscopy (XPS), using the Al/(Al+Si) atomic ratio after ALD as an indicator of Al_2O_3 film growth. Inhibitor **1** (Mw = >5000 g/mol) maintained strong inhibition for at least 50 ALD cycles. For comparison, a short perfluoroalkyl-substituted trialkoxysilane (inhibitor **2**) was examined under the same conditions; its monolayer lost inhibitory effectiveness after approximately 20 ALD cycles. Water contact angle (WCA) measurements showed that inhibitor **1** produced more hydrophobic surfaces than inhibitor **2** (inhibitor **1**: 112.3°, inhibitor **2**: 107.2°). These results indicate that both molecular flexibility and high surface hydrophobicity are key molecular design parameters for inhibitors in AS-ALD processes employing highly reactive precursors such as TMA. Detailed surface characterization data and implications for future inhibitor design in AS-ALD will be discussed.

AS-TuP-6 Area-Selective Growth of HfO_2 Thin Film through a Cyclic Plasma-Enhanced Atomic Layer Process, ***Jun Seo Hwang***, *So Won Kim, Sung Hyun Lim, Hee Chul Lee,* Tech University of Korea

Area-Selective Deposition (ASD) enables the formation of highly precise and uniform patterns through a bottom-up approach and has attracted significant attention as a technology capable of mitigating Edge Placement Error (EPE) issues in 3D device fabrication [1]. Recently, inhibitor-free ASD has been reported using thermal ALD after hydrogen or halogen treatments on amorphous carbon (a-C) surfaces [2]; however, these methods have limitations for in-situ integration with subsequent plasma-enhanced atomic layer etching (PE-ALE) processes. Therefore, in this study, inherent ASD was implemented by applying a PE-ALD/ALE supercycle without additional surface treatment, leveraging the intrinsic non-growth characteristics of a-C.

In this work, Si, SiO_2, and Si_3N_4 were used as growth surfaces (GS), while a-C was used as the non-growth surface (NGS), and the representative high-k material HfO_2 was selectively deposited on the GS regions. X-ray reflectivity (XRR) analysis showed that distinct thickness fringes appeared on the GS regions after 20 cycles, whereas fringe formation on the NGS regions was observed after 50 cycles, indicating cycle-dependent selectivity characteristics. Furthermore, cross-sectional SEM analysis revealed that up to 50 ALD cycles on the NGS region, approximately 7.2 nm of a-C etching, and about 2 nm of HfO_2 deposition occurred simultaneously. This behavior is interpreted as suppression of TEMA-Hf precursor adsorption during the initial ALD adsorption step, while the a-C surface was etched by O_2 radicals generated during the reactant supply step. After performing PE-ALE following 50 ALD cycles, the selectivity between GS and NGS was effectively close to infinity, confirming that surface-selective growth can be induced solely through the PE-ALD/ALE supercycle.

This study suggests that selective deposition can be achieved in the gate oxide deposition step following trench formation in cell transistor structure processes such as RCAT and BCAT, without additional masks or etch-back processes, thereby simplifying the process.

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AS-TuP-7 Inhibition of Hafnia and Alumina Using Silanes, ***Chad Brick,*** 11 Steel Road East

Area–selective deposition (ASD) has grown into an important paradigm in semiconductor process integration in the last decade. By directing film growth to predefined regions, ASD can reduce overall process complexity, decrease reliance on lithographic patterning, and improve dimensional accuracy by preventing overlay–related defects. This approach is particularly advantageous for filling or coating intricate 3D topographies—such as vias and both vertical and horizontal trench structures—where conventional lithography often encounters significant limitations.

While relatively robust information is available on the interaction of silanes with silica surfaces, comparable data with respect to other metal oxides such as hafnia or alumina is sparse. In this study, we demonstrate that relative to a reference SiO_2 deposition process, different silane compounds and inhibition strategies are required for optimal inhibition of silica, hafnia and alumina respectively.

AS-TuP-8 Impact of Aluminum Precursor on Selective Dielectric on Metal Deposition, ***Jiyeon Kim,*** *Dennis Hausmann, Alex Fox,* LAM Research*; Florian Preischel, Harish Parala, Anjana Devi,* Leibniz Institute, IFW Dresden, Germany

Selective deposition of a dielectric film, such as aluminum oxide (Al_2O_3) or hafnium oxide (HfO_2), on metal or metal-oxide surfaces (also known as DoM), without growth on silicon dielectric surfaces, has numerous applications in semiconductor manufacturing. These include the selective deposition of hard masks to enhance dry etch performance. Typical growth surfaces include W, Mo, and Co, with or without their native oxides, whereas inhibited surfaces are usually doped (C, N)-silicon oxides.Typically, this is achieved using small-molecule inhibitors (SMI), such as dimethylaminotrimethylsilane (DMATMS), which selectively chemisorb onto silicon oxide surfaces but not onto metal/metal oxide surfaces. A DMATMS-modified SiO_2 surface exhibits a significant (~2 nm) nucleation delay from AlO_x deposition using dimethylaluminum isoproxide (DMAI)/H_2O, relative to an uninhibited surface. In this work, alternate aluminum precursors and their impact on selectivity are evaluated. Methods for assessing the selectivity failure modes are also examined in this context.

To evaluate the early stages of selectivity performance, we use vapor-phase decomposition mass spectrometry (VPD-MS). This method allows evaluation of film thicknesses as low as <0.0001 nm, enabling the determination and quantification of events during the initial nucleation period. The selectivity and nucleation behavior of several aluminum precursors and inhibitors are evaluated using VPD-MS, alongside ellipsometry and water contact angle (WCA), compared with a baseline process using DMAI/H_2O. Our findings show that selectivity failure is primarily due to the inability of the inhibitor to passivate all potentially reactive sites on the wafer surface, as opposed to the breakdown of the inhibitor or inhibition layer itself.

Figure 1. Comparison of Al_2O_3 ALD growth on the inhibited vs. the non-inhibited surface by the Al atom concentration (left) and the Al_2O_3 film thickness (right).

AS-TuP-9 Tuning Surface Reactivity by Uniform Chemical Modification with Organic Ligands for Area-Selective Processes, ***Andrew Teplyakov,*** University of Delaware

In modern microelectronics, area-selective processes have become the key to produce atomically-precise features. However, in these applications, chemical reactivity and passivation of a surface have to be considered in the context of a specific substrate and a specific deposition chemistry. In addition, surface modification may serve to either promote or suppress the deposition, and for some technological schemes, the ability to switch from non-growth to growth substrate may be needed. That is why small molecule organic modifiers present a challenging but extremely versatile platform to tune surface reactivity even on complex materials. This talk will use model ALD processes with TiO_2 (TDMAT/water and $TiCl_4$/water) or Al_2O_3 (TMA/water) to test the reactivity of modified semiconductor surfaces, targeting organic monolayers with switchable reactivity on silicon substrates and also addressing the uniformity of chemical modification of traditionally unreactive surfaces, like those of 2D van der Waals nanomaterials. These processes will be analyzed by spectroscopic and microscopic methods, and selected results will be evaluated using computational DFT approaches. Although the focus will be on AS-ALD applications, some of the conclusions will also be important to designing atomically precise etching schemes, especially for 2D structures.

AS-TuP-10 Computational and Experimental Approaches to Hydrofluoric Acid-treated SiO_2 and SiNx Surfaces for Area-Selective Atomic Layer Deposition, ***Namkyu Yoo,*** *Sanghun Lee, Tae Hyun Kim, Chanju Lee, Jisang Yoo,* Yonsei University, Korea*; Seung-min Chung,* Hoseo University, Republic of Korea*; Hyungjun Kim,* Yonsei University, Korea

Selective deposition of SiO_2 and SiN_x is a promising approach for advanced 3D NAND fabrication, which consists of oxide–nitride stack architectures for enabling discontinuous charge trap layers. Generally, area-selective atomic layer deposition (AS-ALD) relies on differences in surface functional groups; however, the presence of native oxide on SiN_x obscures these groups and degrades selectivity. Consequently, HF etching is commonly employed prior to deposition, yet its impact on surface chemistry remains controversial and often overlooked.

Therefore, this study investigates how HF treatment alters the surface chemistry of SiO_2 or SiN_x and its subsequent influence on AS-ALD. DFT calculations reveal distinct rate-limiting steps for HF etching of SiO_2 and SiN_x, resulting in Si–OH termination on SiO_2 surfaces and Si–F/Si–NH termination on SiN_x. Furthermore, simulations show that precursor adsorption on fluorine-terminated SiN_x is thermodynamically unfavorable, with an energy barrier exceeding 292.5 kJ/mol. Experimental results show that increasing the HF concentration from 1 % to 10 % raises the fluorine content on SiN_x surfaces from 1 % to 3.3 %, significantly enhancing SiO_2 deposition selectivity. The thickness difference of ALD SiO_2 on oxide and nitride substrates etched by 10 % HF solution was greater than 2 nm.

This work clarifies the kinetics of HF etching and the inhibitory effect of surface Si–F species on precursor adsorption using DFT calculation. Additionally, experimental results confirm that fluorine is present exclusively on SiN_x surfaces after HF treatment and plays a critical role in suppressing nucleation during ALD. These findings elucidate HF induced surface chemistry modifications in oxide and nitride materials and provide insights for achieving reliable area-selective ALD in nanoelectronic device fabrication.

Acknowledgement

This work is funded by the Air Liquide Co. as a precursor supplier.

AS-TuP-11 Influence of Plasma Power and Supercycle Conditions on Selectivity in DIPAS-Based SiO_2 AS-ALD, ***Tae Hwan Lim,*** SK hynix Inc. Korea*; Rui Loureiro, José Fernandes,* International Iberian Nanotechnology Laboratory, Portugal*; Yu Sung Jin, Dong Kyun Lee, Deok Sin Kil, Jung Il Hwang, Sung Gon Jin,* SK hynix Inc., Korea*; Jennifer Teixeira, Pedro Salomé,* International Iberian Nanotechnology Laboratory, Portugal

As 3D NAND technology continues to scale toward higher layer counts and reduced feature dimensions, shrinkage of the oxide/nitride pitch in oxide–nitride–oxide (ONO) stacks has increased susceptibility to parasitic capacitive coupling between neighboring charge trap nitride (CTN) regions. This effect can be further exacerbated by enhanced capacitive coupling between the CTN layer and adjacent metal electrodes, leading to unintended cell-to-cell interference and electrical performance degradation. These challenges highlight the need for precise spatial control in dielectric and CTN deposition processes. Area-selective atomic layer deposition (AS-ALD), which enables material growth exclusively on target surfaces while suppressing nucleation on non-target regions, has therefore emerged as a key enabling technique for next-generation 3D NAND integration. Through this selective deposition approach, physical separation of adjacent CTN regions can be achieved, thereby mitigating cell-to-cell interference and preserving cell characteristics in highly stacked 3D NAND architectures. Accordingly, in this study, SiO_2 AS-ALD was employed to selectively deposit SiO_2 on SiO_2 surfaces while effectively suppressing SiO_2 growth on SiN_x. Specifically, a low-temperature DIPAS/O_3-based SiO_2 ALD

process was developed by leveraging the inherent selectivity of DIPAS toward SiO_2 over SiN_x. Under source-saturated conditions, a reference process was established at 100 °C, yielding a SiO_2 thickness contrast of 1.71 nm between SiO_2 and SiN_x after 50 cycles. Cycle-dependent growth analysis revealed pronounced incubation behavior on SiN_x, extending up to ~20 cycles. To further regulate selective growth, remote plasma pretreatments using N_2, N_2/H_2, and NH_3 were applied prior to DIPAS exposure to modify surface terminations and suppress nucleation. At 100 W, the application of N_2, N_2/H_2, and NH_3 plasmas eliminated the SiO_2 thickness contrast between SiO_2 and SiN_x, indicating plasma-induced surface state equalization. In contrast, at 50 W, a 1:10 supercycle reduced the thickness contrast by 0.27 nm under N_2 plasma, while enhancing it by 0.49 nm under N_2/H_2 plasma. Moreover, a 1:50 supercycle at 50 W maintained the contrast under N_2/H_2 plasma but improved it by 0.43 nm and 0.31 nm under N_2 and NH_3 plasmas, respectively. These trends imply that plasma pretreatments modify surface reactivity, thereby affecting the relative DIPAS nucleation kinetics and incubation behavior between SiO_2 and SiN_x. In summary, these results demonstrate that appropriate tuning of plasma power and supercycle conditions enables the preservation or enhancement of selectivity, defining a viable process window in DIPAS-based AS-ALD.

AS-TuP-12 Alcohol-Mediated Modulation of Surface Chemical States for Inherent Area-Selective Atomic Layer Deposition, ***Kun Cao***, *Weizhen Wang, Boxuan Li, Rong Chen,* Huazhong University of Science and Technology, China

Inherent area-selective atomic layer deposition (AS-ALD) fundamentally relies on a distinct disparity in surface chemical states between growth and non-growth area. For SiO2/Cu patterned architectures, the oxidation of the Cu surface serves as a primary driver for the loss of selectivity as the ALD process proceeds. In this presentation, an alcohol-mediated ASD process is introduced, utilizing alcohols with varying carbon chain lengths to precisely modulate surface chemical states to enhance selectivity. A competitive-synergistic mechanism involving surface reductive capability and steric hindrance is identified as the governing factor for process selectivity. Results demonstrate that while the reducing ability of alcohols on oxidized Cu surfaces diminishes with increasing carbon chain length, their steric hindrance increases. EtOH is identified as the optimal pretreatment agent, yielding an exceptional selectivity exceeding 99.9%. Moreover, the alcohol-mediated ALD process is successfully extended to other oxide systems with precursors bearing analogous ligands, demonstrating the generality of the proposed strategy. This work provides a versatile methodology for manipulating surface redox and physisorption effects to achieve high-selectivity AS-ALD.

AS-TuP-13 Site-Specific and Temperature Dependent Hydration of Faceted Alpha Hematite, ***Asare Dua***, Illinois Institute of Technology*; Luke Nunzio,* Purdue University, USA*; Ashley Bielinski,* Argonne National Laboratory, USA*; Yue Li,* Argonne National Lab*; Cong Liu, Alex Martinson,* Argonne National Laboratory, USA*; Adam Hock,* Illinois Institute of Technology

Alpha hematite (–Fe_2O_3) is an abundant metal oxide whose surfaces and interfaces control key processes in catalysis, sensing, and photoelectrochemistry. While the more stable –Fe_2O_3 (001) surface is well studied, less stable facets such as (012) and (104) which are more relevant in the aforementioned applications due to higher surface activity remain least studied. Surface sites of –Fe_2O_3 (012) and (104), as well as their distinct stability were identified through temperature-dependent hydration by combining in situ infrared reflection absorption spectroscopy (IRAS) with density functional theory (DFT) vibrational analysis.

For α-Fe_2O_3 (012), we found sites that promoted the dissociative and molecular adsorption of D_2O. Dissociatively adsorbed D_2O were either terminal or bridging. In both cases the hydroxyls were either isolated or interacting with nearby species. Protons of bridging hydroxyls (μ_{3a}–OD (isolated); μ_{3b}–OD (interacting with nearby hydroxyls)) are bound to triply coordinated surface oxygens while terminal hydroxyls (μ_{1a}–OD (interacting with nearby hydroxyls)) were bound to octahedral surface Fe atoms (Fe_{oct}^{3+}). Similar to dissociatively adsorbed D_2O, molecularly adsorbed D_2O was either isolated (D_2O_a) or interacting with nearby hydroxyls (D_2O_b).

α-Fe_2O_3 (104) on the other hand exhibited an isolated doubly coordinated bridging hydroxyl (μ_{2a}–OD) and an interacting bridging species (μ_{2b}–OD) rather than triply coordinated bridging hydroxyls. This preference is backed by our DFT calculations which shows triply coordinated bridging hydroxyls were highly unstable on α-Fe_2O_3 (104). Results from IRAS showed two isolated terminal hydroxyls, μ_{1a}–OD and μ_{1b}–OD, were present on the surface of α-Fe_2O_3 (104). This indicates two types of undercoordinated surface atoms existed with the first being undercoordinated tetrahedral Fe atoms (Fe_{tet}^{3+}) since they're the surface atoms of α-Fe_2O_3 (104), while the second is from the second layer of Fe atoms which have octahedral geometry. The undercoordination of Fe_{oct}^{3+}atoms however suggests oxygen vacancies (V_o) were present and some of these might migrate from surface to the second lattice of α-Fe_2O_3 (104). Our temperature dependent studies support this hypothesis since the population of μ_{1a}–OD, μ_{1b}–OD, and μ_{2a}–OD increased with increasing temperature when under vacuum (0.8 torr).

The distinct local environments of the sites on α-Fe_2O_3 (012) andα-Fe_2O_3 (104) and changes in properties with respect to temperature revealed through this work provide a fundamental to tool that may be used to engineer the surface of alpha hematite through site- or facet-selective atomic layer deposition.

AS-TuP-14 Inherently Selective Atomic Layer Deposition of Niobium Oxide Thin Films Using a Novel Precursor, ***Hyun-Kyu Ryu***, *Sung-Woo Ahn, Myeong-Ho Kim, In-Jae Lee, Chae-Young Song, Jin-Sik Kim, Won Yong Koh,* R&D Center UPChem, Republic of Korea

Nb_2O_5 is a promising dielectric material with its relatively high dielectric constant (k≈ 29-60) and wide band gap (~3.6 eV), and its area-selective deposition (ASD) process becomes essential to enable the bottom-up patterning and simplified process integration on nanoscale and 3D DRAM manufacturing.

In this work, we demonstrate a robust ALD process for Nb_2O_5 thin films using a novel Nb precursor, "*UP-Nb*", designed and synthesized by UP Chemical. When evaluated at 300 °C with O_3 as the oxidant, *UP-Nb* exhibited clear self-limiting growth behavior, with a growth-per-cycle (GPC) of approximately ~0.3 Å/cycle as a function of precursor exposure time. X-ray photoelectron spectroscopy analysis of the Nb 3d core-level spectra confirmed a near-stoichiometric Nb_2O_5 composition, indicating chemically stable oxide formation. Furthermore, transmission electron microscopy analysis of high-aspect-ratio (20:1) patterned structures revealed highly conformal film growth, with step coverage exceeding 90%, demonstrating the suitability of the three-dimensional device architecture.

Beyond conventional ALD performance, *UP-Nb* enables inherently selective ALD behavior without the use of molecular inhibitors. Selective Nb_2O_5 growth was observed on TiN surfaces without an incubation delay, while nucleation on SiN substrates was effectively suppressed for up to ~20 ALD cycles. In contrast, a commercially available Nb precursor exhibited incubation-free growth on both TiN and SiN substrates under the same process conditions, indicating the absence of inherent selectivity. This clear distinction confirms that the selectivity originates from the intrinsic precursor–surface reactivity of *UP-Nb* rather than from process conditions. The demonstrated inhibitor-free inherent selectivity, combined with stable ALD characteristics and high conformality, highlights *UP-Nb* as a highly promising precursor for Nb_2O_5 AS-ALD process in next-generation nanoscale and 3D DRAM devices.

AS-TuP-15 Influence of Precursor Molecular Size on Aluminum Oxide Area-Selective Deposition, ***Sharmistha Bhattacharjee***, Lehigh University*; Michelle Paquette,* University of Missouri-Kansas City*; Nicholas C. Strandwitz,* Lehigh University*; Sean King,* Intel Corporation

Area-selective atomic layer deposition (AS-ALD) is a bottom-up strategy for advancing nanoscale fabrication of electronic and functional devices. The effectiveness of AS-ALD is strongly governed by precursor–surface interactions. The factors such as molecular size, steric hindrance, and chemical reactivity determine whether the precursor will diffuse through a blocking self-assembled monolayer (SAM), react with the blocking layer, or react with a defect. Highly reactive aluminum precursors such as trimethylaluminum (TMA) are challenging to employ in AS-ALD due to their small size and high reactivity, which often results in precursor penetration into non-growth regions and subsequent loss of selectivity. Rational optimization of precursor ligand size, structure, and reactivity is therefore essential to suppress precursor infiltration on non-growth surfaces.

Here, we examine a series of alternative Al precursors including TMA, aluminum tri-sec-butoxide, and tri-i-butylaluminum for the growth of Al_2O_3 with H_2O co-reactant.We examined the ability to block the growth of alumina with these precursors using dodecanethiol SAMs on copper over a temperature window of 100 to 160 °C. Film growth and density are evaluated using spectroscopic ellipsometry and X-ray reflectivity measurements. The blocking ability is examined by quantifying Al at% from X-ray photoelectron spectroscopy. Significantly increased blocking was found with the non-TMA precursors. 100% selectivity was sustained for aluminum tri-sec-butoxide, whereas tri-i-butylaluminum maintains selectivity above 90% after 100 ALD cycles of Al_2O_3. This study proves that

combining a less reactive and sterically hindered precursor with a well-ordered SAM provides an effective strategy for maximizing blocking performance in AS-ALD.

ALD Applications

Room Ybor Salons I-IV - Session AA1-WeM

ALD for Memory I

Moderators: Han-Bo-Ram Lee, Incheon National University, **Seung Wook Ryu**, SK hynix

8:00am **AA1-WeM-1 Atomic Layer Deposition in Conventional and Emerging DRAM Devices**, ***Kyooho Jung***, *Jungkyun Kim, Kyung Mee Song, Sunghyun Kim, Donghyun Kim, Sangjun Lee, Jeonggyu Song, Sangwook Kim,* Samsung Advanced Institute of Technology, Republic of Korea **INVITED**

Atomic Layer Deposition (ALD) has become an indispensable technology in the semiconductor industry due to its excellent conformality, step coverage, film quality, and precise thickness control. This presentation introduces ALD process developments and device characterizations conducted at Samsung for both conventional and emerging DRAM technologies.

In conventional DRAM, capacitors represent one of the most critical application areas for ALD. The primary objectives for capacitors include achieving a high dielectric constant, low bulk and interfacial defect densities, excellent step coverage, and reduced mechanical stress-induced failures. These requirements can be addressed through careful optimization of the ALD process and thin-film stack design. This talk will present several approaches we have employed to improve dielectric constant, leakage current characteristics, and mechanical stress in DRAM capacitors.

For emerging DRAM devices, we will introduce our recent work on oxide semiconductor vertical channel transistors (VCTs), 1TnF DRAM, and 1T ferroelectric FETs (3D FEFETs). ALD plays a key role in these technologies owing to its superior thickness uniformity, precise interface and layer control, and compatibility with complex 3D structures. This presentation will discuss both the device performance and material properties of ALD-based films implemented in these emrging DRAM devices.

8:30am **AA1-WeM-3 Sacrificial Atomic Layer Deposition for Nanostructured Chalcogenide Materials**, ***Chanyoung Yoo***, Hongik University, Republic of Korea

Atomic layer deposition (ALD) offers unique advantages for conformal and thickness-controlled growth of functional materials. However, extending ALD to chalcogenide materials remains fundamentally challenging due to severe surface oxidation, limited precursor compatibility, and the tendency toward island growth and phase separation. These issues become more pronounced when targeting low-dimensional, metastable, or superlattice chalcogenide structures required for next-generation memory and neuromorphic devices.

In this presentation, we introduce sacrificial atomic layer deposition (S-ALD) as a general and scalable growth paradigm for nanostructured chalcogenide materials. The key concept of S-ALD is the deliberate incorporation of a sacrificial layer that temporarily mediates metal–chalcogen bonding during ALD cycles and is selectively removed in a subsequent step [1]. This sacrificial process effectively suppresses parasitic oxidation, mitigates ligand incompatibility, and enables controlled chalcogen rearrangement, thereby facilitating the deposition of highly uniform, fully substrate-covering crystalline chalcogenide films with growth behavior approaching layer-by-layer deposition.

By applying S-ALD, we demonstrate several representative chalcogenide systems that are difficult to realize using conventional approaches. These include top-to-bottom local epitaxial growth of two-dimensional Sb_2Te_3 enabled by controlled sacrificial layer removal [1], melt-quenching-free Sb_2Te_3/GeTe superlattice phase-change films with well-defined interfaces [2], and ultrathin monatomic antimony [3] and tellurium films with atomic-level thickness control. Structural and spectroscopic analyses reveal that S-ALD promotes uniform, layer-by-layer growth even at reduced deposition temperatures. The versatility of S-ALD highlights its potential as a unified platform for engineering low-dimensional and three-dimensional chalcogenide architectures. This approach provides new opportunities for conformal integration of phase-change materials, ferroelectric–chalcogenide heterostructures, and emerging nanoelectronic devices, where precise control over phase, thickness, and crystallinity is essential.

[1] C. Yoo et al., *Chem. Mater.*, 35, 17, 7311 (2023)
[2] C. Yoo et al., *Adv. Mater.*, 34, 50, 2207143 (2022)
[3] G. Jeon et al., Adv. Mater., e19924 (2025)

8:45am **AA1-WeM-4 Enhancing Dielectric Properties of ALD Al-Doped HfO_2 Films for Memory Applications: The Role of Homogeneous Aluminum Distribution**, ***Son Hoang***, *Larry Chen, Charlene Chen, Randall Higuchi, Vijay Narasimhan, Liana Alves,* EMD Electronics*; Zeyuan Ni,* STDC, Tokyo Electron Technology Solutions Ltd, Japan*; Atsushi Kubo,* STDC, Tokyo Electron Technology Solutions Ltd., Japan

The stabilization of non-monoclinic phases including tetragonal and orthorhombic of HfO2 in ultrathin films (<6 nm) is essential for enhancing permittivity and ferroelectricity, which are critical for DRAM capacitors and emerging non-volatile memory technologies such as ferroelectric tunnel junctions (FTJs) and ferroelectric field-effect transistors (FeFETs). Previous studies have shown that incorporating Al dopant can effectively stabilize these non-monoclinic phases [1,2,3]. The ALD investigations typically employed an atomic layer deposition (ALD) supercycle of HfO2 and Al2O3 with varying HfO2/Al2O3 cycle ratios to modulate the Al concentration in the Al-doped HfO2 films. However, a 6 nm Al-doped HfO2 film generally requires only 1 or 2 Al2O3 cycles to achieve the narrow optimal Al concentration window of 3-5 atomic percent, resulting in highly localized Al distribution. This presents a critical gap in understanding the effects of Al dopants in ALD compared to physical vapor deposition (PVD) or theoretical studies, which assume homogeneous Al distribution in HfO2 films [3].

In this work, we demonstrate that achieving a homogeneous distribution of Al in ALD Al-doped HfO2 thin films (<60 Å) is crucial for optimizing performance in advanced memory applications. We employed a Hf-Al-Oxidant (Hf-Al-O) ALD method, wherein the Al precursors selectively adsorb onto unoccupied sites left after hafnium precursor exposure. This selective adsorption leads to a three-fold dilution of Al incorporation into HfO2, resulting in a more uniform Al dopant depth profile while preventing the formation of continuous Al2O3 layers that can hinder crystallization, as often seen in conventional HfO2/Al2O3 supercycle approaches. The Hf-Al-O method produced Al-doped HfO2 films with 100% non-monoclinic phases, compared to only 50% in HfO2/Al2O3 supercycle processes. Furthermore, metal-insulator-metal capacitors fabricated with these films exhibited a dielectric constant increase from 19 to 27, a reduction in leakage current by 1.5 orders of magnitude relative to pure HfO2 films, and excellent ferroelectric properties with 2Pr window of 15–20 $\mu C/cm^2$.

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9:00am **AA1-WeM-5 Germanium Doping for Electrical Modulation of Ferroelectric HZO Using Atomic Layer Deposition**, ***Jared McWilliams***, EMD Electronics, USA

Since its first discovery, ferroelectricity in hafnia-based oxides has seen significant improvement using the large-scale, manufacturing-friendly atomic layer deposition (ALD) method, making them the most promising candidate for advancing non-volatile memory technology. Among all compositions, the 1:1 ratio alloy $HfZrO_2$ (HZO) is the most studied compound due to the low thermal budget required to achieve satisfactory electrical performance. However, the high operating voltage of HZO,resulting in high energy dissipation and device early failure, hinders its further technical adoption. Significant efforts have been invested in understanding switching mechanisms and predicting potential dopant candidates to reduce the coercive voltage of HZO.

This work demonstrates, for the first time, the experimental validation of Germanium-doped HZO since the theoretical prediction by Chae *et al.* [1]. Electrical behaviors such as polarization switching, leakage, and voltage-dependent capacitance are taken into account along with physical characterizations to elucidate the mechanisms behind the ferroelectric switching and the reduction in the coercive field of Ge-doped HZO. Different doping strategies to achieve desirable ferroelectric characteristics are also presented, highlighting the importance of dopant concentration and the location of dopant atoms within the device stack. The advantage of using precursors with wide ALD windows is also discussed to emphasize further the role of precursor choices in maintaining a low thermal budget for the fabrication process of doped HZO.

9:15am **AA1-WeM-6 Design of Interface Formation Process for Superior Ferroelectricity and Enhanced Fatigue Resistance in $Hf_xZr_{1-x}O_2$-Based Ferroelectric Devices**, ***Takashi Onaya***, *Toshihide Nabatame, Takahiro Nagata, Kazuhito Tsukagoshi,* National Institute for Materials Science, Japan

Ferroelectric $Hf_xZr_{1-x}O_2$ (HZO) has been extensively studied due to the maturity of its atomic layer deposition (ALD) process and its low thermal budget below 400°C. However, fatigue, which is degradation of switching polarization (P_{sw}) during field cycling, remains a critical issue for practical applications. We previously reported that the primary origin of fatigue is the electric-field-induced interface reaction between the HZO film and the TiN electrode, which leads to the formation of additional oxygen vacancies in the HZO film [1]. To suppress this interface reaction, we focused on interface formation processes of inserting an oxygen blocking interfacial layer (IL) at the HZO/TiN interface. In this work, we investigated the ferroelectricity and fatigue properties of HZO films by inserting ILs.

First, the TiN/HZO/TiN capacitor with the surface-oxidized TiN bottom-electrode (w/ Oxid.-BE-TiN) was fabricated by O_2 plasma treatment of the BE-TiN surface in the ALD chamber, following by continuous deposition of the ALD-HZO film without vacuum break. The oxygen-rich TiO_xN_y-IL was formed for the w/ Oxid.-BE-TiN capacitor at the HZO/BE-TiN interface evaluated by XPS analysis. For the endurance properties, no significant difference in P_{sw} in the pristine state was observed between the capacitors without (w/o) and w/ Oxid.-BE-TiN due to almost the same crystal structure of both HZO films evaluated by XRD patterns. In the fatigue state, on the other hand, the P_{sw} degradation of the w/ Oxid.-BE-TiN capacitor was suppressed by ~14% compared to that of the w/o capacitor. This could be because the oxygen-rich TiO_xN_y-IL plays a critical role as an oxygen blocking IL, which suppresses the interface reaction at the HZO/BE-TiN interface.

Next, ALD-ZrO_2 nucleation layers (NLs), which promote the ferroelectric orthorhombic (O) phase formation in HZO films [2], were employed as oxygen blocking ILs. The HZO film for TiN/ZrO_2/HZO/ZrO_2/TiN (w/ ZrO_2-NL) capacitor formed more O phase compared to the TiN/HZO/TiN (w/o) capacitor, resulted in 2.3 times higher P_{sw} in the pristine state. For the fatigue state, furthermore, the w/ ZrO_2-NL capacitor exhibited less P_{sw}degradation (~33%) compared to the w/o capacitor (~52%). Therefore, it was found that the ALD-ZrO_2-NLs are effective not only in enhancing P_{sw} but also in suppressing fatigue by acting as an oxygen-blocking IL.

These experimental results indicate that careful design of the HZO/electrode interface is crucial for achieving high P_{sw} and high fatigue resistance simultaneously in HZO-based ferroelectric devices.

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9:30am **AA1-WeM-7 Low-Temperature ALD HfO_2 for Magneto-Ionic Applications**, ***Alessandro Cataldo***, Politecnico di Milano, Italy*; Sabina Spiga,* Consiglio Nazionale delle Ricerche (CNR-IMM), Italy*; Himadry Nandan Mohanty, Alan Durnez,* Centre de Nanosciences et de Nanotechnologies (C2N), France*; Andrea Li Bassi,* Politecnico di Milano, Italy*; Seyed Ariana Mirshokraee,* Consiglio Nazionale delle Ricerche (CNR-IMM), Iran (Islamic Republic of)*; Liza Herrera Diez,* Centre de Nanosciences et de Nanotechnologies (C2N), France*; Alessio Lamperti,* Consiglio Nazionale delle Ricerche (CNR-IMM), Italy

Voltage-controlled magneto-ionic devices rely on oxide-based functional layers capable of enabling low-power operation, reversible mechanisms, cyclability, and stable interfacial coupling with ferromagnetic (FM) materials. In this framework, hafnium dioxide (HfO_2) has emerged as a key enabling material to control the channel gating in metaplastic spintronic synapses and to sustain the electric field for the ion migration [1-2]. Among the deposition techniques, atomic layer deposition (ALD) offers precise thickness control, conformality, and atomic-level tunability, making it a privileged approach for synthesizing HfO_2 films [3]. However, the integration of oxides with FM materials for such applications requires low-temperature (low-T) processing to avoid interfacial and magnetic properties degradation [4-5]. Moreover, the functionality of these devices is linked with the content and mobility of ions which migrate towards the ferromagnet via gating applications. Therefore, a controlled defectivity through an engineered ALD growth is fundamental. In this work, we investigate the growth of HfO_2 via ALD using TEMAHf and H_2O over a temperature range from 200 °C to 80 °C, focusing on engineering the H_2O semi-cycle to tailor the defectivity, and on the correlation between growth process and physical, chemical and electric properties.

A progressive reduction of the deposition temperature leads to a marked increase in the growth-per-cycle (GPC) from 0.82 Å/cy at 200 °C to 1.34 Å/cy at 80 °C. XPS measurements confirm a consistent Hf^{4+} chemical state, while the O/Hf atomic ratio evolves from 1.98 at 200°C to a minimum of 1.8 at 80°C. Furthermore, OH- content is seen to increase significantly for growth temperatures below 100°C. ToF-SIMS profiling confirms an increment of OH- species and highlights an almost constant concentration of carbon-related contaminants, indicating a selective incorporation of functional OH- groups. C-V measurements on MIM devices report a dielectric constant $k \approx 17 \pm 1$ independently on the growth temperature of the integrated HfO_2, proving the high quality despite the thermal budget reduction. However, breakdown voltage analysis shows that a reduced growth temperature deeply affects the sub-conductive behaviour of the grown oxide as well as the dielectric breakdown, showing a E_{BD} shift from 3 MV/cm to 4.5 MV/cm for V^+.

The results demonstrate that engineered low-T ALD HfO_2 can achieve the combination of high dielectric performance, controlled ionic content, and interface compatibility required for magneto-ionic devices such as spintronic synapses for advanced computing architectures.

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Financial support from EIC Pathfinder METASPIN project (Grant n. 101098651).

9:45am **AA1-WeM-8 High-mobility Atomically Ordered IGZO Transistors Deposited by Thermal Atomic-Layer-Deposition**, ***Min-Seo Kim***, *Seong-Hwan Ryu,* Hanyang University, Korea*; Yoon-Seo Kim,* IMEC, Belgium, Republic of Korea*; Jin-Seong Park,* Hanyang University, Korea

As silicon-based devices approach fundamental scaling and integration limits, oxide semiconductors have attracted increasing attention as channel materials for next-generation memory and logic technologies requiring three-dimensional architectures and back-end-of-line (BEOL) compatibility. In advanced DRAM systems, high-mobility channels are essential to secure sufficient driving current and sensing margin, while in logic and monolithic three-dimensional (M3D) integration, minimizing the mobility mismatch between silicon and oxide transistors is critical to suppress bandwidth bottlenecks during inter-tier communication. Although amorphous InGaZnO (IGZO) offers excellent processability and uniformity, its carrier transport is inherently limited by disordered bonding networks, motivating structural strategies to overcome the mobility ceiling of amorphous oxides. Atomic layer deposition (ALD) provides a powerful platform for such structural engineering owing to its angstrom-level thickness control and precise regulation of interfacial reactions. In oxide nanolaminate systems, confining carrier transport within In_2O_3-dominant layers and inducing two-dimensional electron gas (2DEG)-like conduction at oxide–oxide interfaces has been proposed as an effective route toward mobility enhancement. However, realizing electronically active interfaces in amorphous systems critically requires atomically controlled layer stacking and chemically complete reactions during growth.

In this study, we demonstrate thermal atomic-layer-deposited atomically ordered IGZO (AO-IGZO) thin films exhibiting ultra-high mobility through 2DEG-like interfacial conduction. By systematically varying the deposition temperature, we identify 250 ℃ as an optimal growth condition where impurity suppression and interfacial ordering are simultaneously achieved. X-ray reflectivity and diffraction analyses reveal the formation of an amorphous yet atomically ordered superlattice-like structure composed of periodically modulated In_2O_3-rich conducting layers and GaZnO barrier layers. Such ordering is absent at lower temperatures due to incomplete precursor reactions and is degraded at higher temperatures where nanolaminate periodicity is disrupted. Top-gate thin-film transistors incorporating the 250 ℃ AO-IGZO channels exhibit a field-effect mobility of approximately 113 cm^2/Vs, far exceeding that of conventional amorphous IGZO devices. This enhanced transport is attributed to carrier confinement at the In_2O_3/GZO interface, which promotes 2DEG-like conduction and effectively circumvents bulk amorphous scattering. These results establish thermal ALD as a viable route for realizing atomically ordered amorphous oxide semiconductors with exceptional mobility, offering a scalable pathway toward high-performance oxide transistors for advanced semiconductor integration.

ALD Applications
Room Ybor Salons I-IV - Session AA2-WeM

ALD for Memory II

Moderators: Ji Hwan Ahn, POSTECH, **Andrea Illiberi**, ASM

10:45am **AA2-WeM-12 Upper-Layer-Induced Crystallization of Metastable Rutile TiO_2**, ***Jihoon Jeon***, *Seung keun Kim,* Korea Institute of Science and Technology (KIST), Republic of Korea

The relentless scaling of dynamic random-access memory (DRAM) technology shrinks capacitor dimensions, thereby degrading charge retention time and triggering read instabilities. This drives the demand for high-permittivity dielectrics that surpass conventional HfO_2 or ZrO_2. Rutile TiO_2, with orientation-dependent permittivity ranging from 80 to 170, emerges as a compelling candidate. However, rutile TiO_2 is metastable under atomic layer deposition (ALD) conditions and requires elevated crystallization temperatures, which pose barriers to integration. Established ALD strategies stabilize rutile TiO_2 by employing lattice-matched bottom electrodes such as RuO_2, IrO_2, SnO_2, or MoO_2. Yet these approaches necessitate either replacing the bottom electrode or introducing additional rutile phase–inducing layers, thereby complicating compatibility with DRAM process flows. Moreover, the industry-standard TiN electrode, lacking lattice matching with rutile TiO_2, remains incompatible with such stabilization routes.

Here, we report for the first time the formation of crystal structure induced by an upper-layer during post-deposition crystallization. This upper-layer-driven templating effect provides a new pathway to control phase selectionin ALD-grown TiO_2thin films. After inducing rutile crystallization, the upper layer can be selectively removed without affecting the underlying structure, leaving a fully crystallized rutile TiO_2. This strategy enables the integration of high-k rutile TiO_2 while preserving the TiN bottom electrode, thereby ensuring full compatibility with DRAM fabrication processes

11:00am **AA2-WeM-13 Surface-Reaction-Energetics-Driven Stabilization of Rutile TiO_2 at Low Temperatures in Atomic Layer Deposition**, ***Seungwan Ye***, *Jihoon Jeon, Jongseo Kim, Seong Keun Kim,* Korea Institute of Science and Technology (KIST), Republic of Korea

As the physical dimensions of dynamic random-access memory (DRAM) continue to scale down, maintaining sufficient charge capacitance has emerged as a key challenge for next-generation memory technology. Therefore, to overcome the limitations of current Zr-based dielectrics, high-k materials with a higher dielectric constant are essential. Among them, rutile TiO_2 is the most promising dielectric due to its high dielectric constant ($k > 80$).

However, the rutile phase of TiO_2 is thermodynamically metastable, typically requiring high temperature process above 600℃, which exceeds the thermal budget for the DRAM fabrication process. Although using lattice-matched rutile bottom electrodes such as RuO_2, IrO_2 and MoO_2 has been proposed to form rutile TiO_2 at low temperatures, their poor process compatibility with the industry-standard TiN bottom electrode remains a critical obstacle.

In this study, we propose a novel method using surface reaction during ALD that enables the growth of metastable rutile TiO_2 thin films at a low temperature of approximately 330℃, irrespective of the bottom electrode. This breakthrough allows for the successful deposition of high-quality rutile TiO_2 on various substrates, including the industry-standard TiN, thereby dramatically enhancing its commercialization potential for next-generation memory devices.

11:15am **AA2-WeM-14 Magnetism of Ultrathin TiO_2 Films Prepared by Atomic Layer Deposition**, ***Jhonatan Rodriguez Pereira***, *Jan Macak,* University of Pardubice, Czechia

Semiconducting oxides are gaining attention for spintronic applications due to their tunable electronic and magnetic properties.[1,2] Among them, TiO_2 is a widely studied semiconducting oxide for a wide range of applications owing to its chemical stability, wide band gap and versatile functionality.[3-5] The observation of room-temperature ferromagnetism in undoped TiO_2 films has raised fundamental questions regarding its origin, which has been frequently linked to intrinsic defects, reduced dimensionality, and interface effects rather than conventional magnetic doping.[6-8] Several studies addressing this phenomenon have focused on films prepared by pulsed laser deposition.[9-11] Given the strong sensitivity of defect-induced magnetism to film thickness and interface quality, a deposition method enabling atomic-scale control is particularly desirable. Atomic Layer Deposition (ALD) provides an ideal platform to address this necessity, owing to its precise control over thickness and composition, as well as its ability to produce smooth and conformal ultrathin films.

In our recent paper, [12] we showed for the first time the ALD growth of ultrathin TiO_2 films (below 10 nm) on $LaAlO_3$ substrates. Structural characterization confirmed the formation of anatase TiO_2 films. Magnetic measurements revealed a pronounced thickness-dependent behavior, with ferromagnetic responses observed for films of intermediate thickness, while thinner films remained diamagnetic. The magnetic signal was strongly anisotropic and confined to the film plane, suggesting a two-dimensional origin associated with surface and interface effects. Complementary chemical and computational analysis indicate the presence of oxygen-related defects, whose concentration varies with film thickness.[12]

The presentation will introduce and describe the ALD growth of ultrathin TiO_2 films, together with their structural, chemical, magnetic, and theoretical characterization, and will discuss the role of defects and interfaces in the emergence of ferromagnetism.

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11:30am **AA2-WeM-15 Low-Temperature Peald of Silicon Nitride Using Diiodosilane for High-Conformality Spacers of Three-Dimensional Memory Devices**, ***Jiabao Sun***, *Tielu Liu, Xin Zhang, Gang Song, Hongbo Sun, Baodong Han, Chao Tian, Chao Zhao,* Beijing Superstring Academy of Memory Technology, China

Silicon nitride (SiN_x) thin films are critical insulating spacers for next-generation high-density memory devices[1]. Transitioning to extreme 3D stacking with deep lateral pockets imposes rigorous demands on plasma-enhanced atomic layer deposition (PEALD)[2]. Specifically, maintaining high-quality films at low thermal budgets is vital for integration with temperature-sensitive amorphous oxide channels. In this work, we investigate a low-temperature PEALD SiNx process using Diiodosilane (DIS, SiH_2I_2). The selection of DIS is motivated by the low dissociation energy of the Si-I bond (~284 kJ/mol)[3], which facilitates efficient precursor activation and surface reactions at reduced temperatures compared to chlorinated or aminated silanes.

We report a comprehensive optimization to address two critical research questions: the achievement of high lateral conformality and the spatial uniformity of the wet etch rate (WER) across complex 3D geometries. A significant reduction in the WER (30:1 HF) of the SiN_x films is achieved, dropping from ~120 nm/min to ~3 nm/min via precise plasma chemistry modulation (Fig. 1). A strong positive correlation between WER and growth per cycle (GPC) indicates that high-growth regimes are associated with plasma-induced damage and reduced film density. X-ray Photoelectron Spectroscopy (XPS) analysis revealed that high WER correlates with a shift in nitrogen bonding environments, specifically the presence of sub-stoichiometric NSi_2O and $NSiO_2$ species over the preferred NSi_3 configuration (Fig. 2). Furthermore, a distinct I peak is identified in high-WER samples, indicating that unreacted precursor fragments at high radiofrequency (RF) power and H_2 flow rates degrade the structural integrity of the film.

To address 3D integration challenges, we achieved ~94% lateral conformality within high-aspect-ratio structures (Fig. 3). Reducing the process pressure from 22.5 Torr to 4 Torr increases the molecular mean free path, enhancing precursor diffusion into deep features. Additionally, minimizing RF power reduces ion directivity, promoting the conformal profile essential for lateral coverage. Notably, the WER within the confined side-pockets was reduced by approximately one order of magnitude, achieving exceptional spatial uniformity across the 3D architecture (Fig. 4). These optimizations provide a robust process window for subsequent Wet etch or Certas gas etching, ensuring structural integrity in 3D integration. This study provides a viable pathway for high-quality SiN_x spacers in temperature-sensitive 3D memory architectures.

Reference

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11:45am **AA2-WeM-16 A Nanolaminate Cushion Approach for Stabilizing Ultrathin Al_2O_3 and SiO_2 Dielectrics in Future Logic and Memory Technologies**, *Mahesh Nepal, Tanka Bhushal,* ***Tara Dhakal,*** Binghamton University

Continued scaling of DRAM capacitor dielectrics and emerging memory devices requires ultrathin insulating layers that maintain low leakage and high reliability. Comparable challenges are also present in embedded and BEOL decoupling capacitors, where capacitance density and electrical stability are critical. However, once oxide dielectrics reach the few-nanometer regime, leakage increases dramatically and breakdown margins collapse, making dielectric reliability a primary limiter to further scaling. Here, we present a novel dielectric stabilization strategy using an atomic layer deposited (ALD) Al_2O_3/TiO_2 nanolaminate engineered to function as a controlled conductive "cushion" interlayer that enables reliable scaling of ultrathin dielectric films.

Spectroscopic analysis using hard X-ray photoelectron spectroscopy indicates oxygen-deficient TiO_2 and compositionally modified Al_2O_3 networks, producing a quasi-conductive nanolaminate that suppresses catastrophic dielectric failure. Electrical impedance measurements confirm that while the nanolaminate exhibits non-ideal dielectric characteristics independently, integration with ultrathin capping dielectrics restores stable capacitive behavior.

Using planar metal–insulator–metal capacitor test structures, we demonstrate that an optimized nanolaminate period enables scaling of Al_2O_3 dielectrics to ~3 nm while achieving leakage current densities near 10^{-7} A/cm^2 at 1 V and capacitance densities approaching 20 fF/um^2 across large-area devices. The stabilization approach is further shown to be transferable to SiO_2-based dielectric stacks, indicating broader material compatibility.

From a memory-scaling perspective, modeling suggests that integration with three-dimensional capacitor geometries could significantly amplify capacitance density, positioning this cushion-enabled architecture as a promising pathway for next-generation DRAM applications. More broadly, this work demonstrates how intentionally engineered leaky nanolaminates can serve as functional interfacial layers to overcome reliability bottlenecks in aggressively scaled dielectric stacks.

ALD Fundamentals: Growth and Characterization
Room HB Plant Ballroom - Session AF1-WeM

Plasma Enhanced and Low Temperature ALD

Moderators: Jolien Dendooven, Ghent University, Belgium, **Mikko Ritala**, University of Helsinki

8:00am **AF1-WeM-1 Understanding Temporal Behavior of Adsorption and Desorption in ALD via Multiple Injections of Precursor**, ***Yu-Sen Jiang,*** Stanford University*; Miso Kim,* Standford University*; Yukio Cho,* Stanford University*; Stacey Bent,* Standford University

Atomic layer deposition (ALD) is renowned for its self-limiting characteristics, enabling precise atomic-level control and high conformality. During an ALD half-cycle, precursors may adsorb onto the substrate as physisorbed species before reacting with surface ligands to chemisorb. However, even under nominally saturated conditions, full surface coverage may not be achieved due to phenomena such as steric hindrance or retention of excess physisorbed precursors. To address this limitation, multiple precursor injections within a single half-cycle are employed to increase the amount of chemisorbed precursor. The observation that ALD growth differs when performed with discrete injections compared to a single injection suggests that adsorbed precursors undergo dynamic behavior on the timescale of a pulse. The temporal effects of precursor adsorption, rearrangement and desorption have received less attention in ALD, for which a single precursor pulse is typically assumed to be fully saturating.

In this work, ALD of HfO_2 with multiple-pulse sequencing was used to elucidate fundamental ALD mechanisms. A single long pulse of Hf precursor (tetrakis(dimethylamido)hafnium, TDMAH) was divided into several shorter sub-pulses to enable a direct comparison between single and multiple pulses during ALD with water as the counteractant at 200°C. The HfO_2 films grown by multiple pulse injection show a 26 % higher growth per cycle, as well as increased grain size, film density, and crystallinity. The improvement is attributed to a denser surface arrangement enabled by staggered precursor exposure. *In situ* infrared spectroscopy reveals differences in the types of hydroxyl groups consumed by precursors between single and multiple pulse modes. Hydroxyl species that were difficult to react in a single pulse (e. g. hydrogen-bonded OH) became more accessible through the multiple feeding of precursors.

To isolate the contribution from each pulse, the Zr precursor (tetrakis(dimethylamido)zirconium, TDMAZ) was introduced into the TDMAH pulse sequence as a "chemical tag" in HfO_2 ALD for defining the specific pulse. This approach enables direct observation of the fractional growth contribution from individual pulses under different pulse-time and pulse-sequence combinations. The results of X-ray photoelectron spectroscopy and *in situ* ellipsometry measurements between 150°C to 220°C indicate that during short pulses, only ~50% of the total growth occurs during the first pulse, resulting in a more sparsely populated surface that allows additional precursors to react in later pulses. Our results reveal that precursor residence time scales with precursor population, implying a coverage-dependent desorption mechanism. Low precursor loading, especially in the unsaturated regime, facilitates desorption and surface rearrangement, thereby enhancing the benefits from multiple-pulse strategy. Further mechanistic analysis of the single versus multiple pulse ALD schemes will be discussed.

8:15am **AF1-WeM-2 Improved Atomic Layer Deposition of Ultra-Thin HfO_2 Dielectrics on Transition Metal Dichalcogenide Surfaces via Low Impact Plasma Pretreatments**, ***Rebecca Dawley,*** University of Michigan*; Sudarat Lee, Wouter Mortelmans, Scott Clendenning,* Intel Corporation*; Ageeth Bol,* University of Michigan

2D transition metal dichalcogenides (TMDs) have shown to be promising candidates as alternative channel materials within scaled transistors in next generation electronics. As transistor dimensions continue to shrink and advanced device architectures evolve, there exists a need for the deposition of high quality, ultra-thin dielectrics onto semiconducting channels, typically via atomic layer deposition (ALD). However, deposition on pristine TMD basal planes is challenging due to the lack of dangling bonds and defect sites typically acting as ALD nucleation sites, thus resulting in nonuniform dielectric coverage.

In this work, we explore the effect of mild (low power, high pressure) H_2S plasma pretreatments to improve HfO_2 ALD on mono and few layer TMDs. First, we evaluate the effect of various plasma exposure duration times on monolayer WSe_2 at 250 °C. Minimal impact to WSe_2 following plasma exposure was confirmed via Raman, X-ray photoelectron, and photoluminescence spectroscopy. These plasma exposures were then applied to WSe_2 prior to ~ 3nm HfO_2 atomic layer deposition resulting in a significant improvement in dielectric nucleation and coverage on WSe_2 basal planes as compared to untreated control samples. To better understand the interplay between the plasma-pretreatment of the WSe_2 surface and the HfO_2 ALD process, we investigated the influence of the precursor (both Hf and O) dose times, number of precursor pulses, purge time, and stop flow pumping schemes on the microstructure of the HfO_2 deposited on pre-treated WSe_2. AFM, backscattered electron imaging, and Auger spectroscopy were utilized to determine an optimal combination of plasma exposure and HfO_2 ALD process parameters to yield uniform dielectrics across TMD basal planes.

After process optimization, we evaluated the minimum possible HfO_2 thickness allowed via our plasma pretreatment strategy while still maintaining fully coalesced films using AFM and cross-section TEM. Electrical measurements will demonstrate the capabilities of our technique in depositing high quality, ultra-thin dielectrics onto TMDs with minimal impact on TMD structural properties. This work will further enable the advancement of TMD based top gate and gate all around transistors with ultrathin dielectrics and addresses the concern of maintaining the integrity of underlying TMD channels during pre-treatments prior to ALD.

8:30am **AF1-WeM-3 Comparing HfO_2 Thin Films Grown by Low-temperature Thermal and Plasma ALD for Neuromorphic Functionality**, *Alessandro Cataldo,* CNR-IMM, Italy*; Alan Durnez, Himadri N. Mohanty,* CNRS-C2N, France*; Seyed Ariana Mirshokraee, Sabina Spiga,* CNR-IMM, Italy*; Liza Herrera-Diez,* CNRS-C2N, France*;* ***Alessio Lamperti,*** CNR-IMM, Italy

The need for integration of materials in the fabrication of devices sensible to thermal budgets, such as in flexible, organic and bio-inspired electronics, requires the development and study of low thermal ALD processes. On this scope several attempts have been performed to tackle this issue from

different sides, involving the development of innovative precursors and engineering of growth processes, including the extension of ALD regime down to 80 °C in thermal ALD or employing plasma ALD to deliver the energy required for the chemical reactivity.

In this context, HfO_2 has been, and still is, the subject of many efforts, driven by the need of both innovative scientific challenges and functionalities and the existing markets. Recently, its integration in neuromorphic and magnetoionic devices, shifted the attention from qualifying the material properties in terms of compact, dense, defect-free, crystalline films, to consider the type and degree of defects, the selective incorporation of additional elements, typically C, N and OH, in amorphous films. Thus, the need to redefine low temperature ALD processes targeting HfO_2 with such specifications.

Within this framework, here, we compare three processes where thermal or plasma ALD is considered, employing two different equipment. In details, we consider TEMAHf and TDMAH as Hf precursors, H_2O as oxidant in the thermal ALD processes or Oxygen from O_2 in 300 W plasma ALD process, with temperature in the 80 – 100 °C range. We target four HfO_2 thickness, 3, 5, 10 and 20 nm, grown on SiO_2/Si substrate, to have the minimal set for accurately verify the ALD window regime and compare any change in the growth per cycle.

Grown HfO_2 layers are characterized from XRR, XPS and ToF-SIMS to evaluate any change in the electron density, elemental chemistry and stoichiometry. We observe, depending on the growth process, a stoichiometry below the nominal O:Hf=2:1 ratio in all cases, the lowest value in HfO_2 films grown using plasma ALD, with a slight evolution of the stoichiometry with the film thickness. Further, we observe from XPS a significant amount of OH groups depending on the ALD process, in-line with the electron density value from XRR. We explain such changes in terms of purging time and engineering of the oxidant sub-cycle within each ALD cycle, and considering the interplay between oxidation and hydroxilation phenomena.

Further, we integrate HfO_2 films in simple MIM capacitors to extract their dielectric constant (k) and voltage breakdown (V_{BD}). k value results around 17 in HfO_2 films from thermal ALD lowering to k = 12 in HfO_2 from plasma ALD, while V_{BD} varies in the range 3.0-5.5 MV/cm. We tentatively explain such changes in terms of defectivity and ionic species inside the grown HfO_2 films.

Finally, we briefly report on how the so-grown HfO_2 films enable, or not, magnetoionic functionality, depending on the ALD process employed.

Financial support from EIC METASPIN project, grant n. 101098651.

8:45am **AF1-WeM-4 Germanium Oxide with Tunable Composition Using Low-Temperature PEALD***, **Florian Preischel**,* Leibniz Institute for Solid State and Materials Research, Germany*; Karl Rönnby, Michael Nolan,* Tyndall National Institute, University College Cork, Ireland*; Harish Parala, Anjana Devi,* Leibniz Institute for Solid State and Materials Research, Germany

Germanium dioxide (GeO_2) is of particular interest in advanced microelectronics and is regarded as an ultrawide bandgap (UWBG) material for next-generation CMOS applications. With exceptional carrier mobility, it shows promise for high-frequency and high-power electronics,[1,2] while its optical properties make it appealing for, e.g., anti-reflection coatings.[3] Furthermore, two-dimensional (2D) GeO_2 has an inherently porous structure with molecular-sized holes and is thus of interest as a material for selective gas-separation membranes.[4,5]

To transition these applications from research to industrial applications, it is necessary to develop scalable processes that enable the deposition of high-quality, defect-free GeO_2 films. Owing to its self-limiting nature, ALD emerges as the most promising solution, offering precise control over thickness and morphology. Yet, ALD strongly relies on the underlying chemistry, and especially the development of low-temperature processes is currently restricted by the lack of suitable Ge precursors.

To address this challenge, we introduce tetrakis-(3-dimethylamino)propyl germanium(IV) [$Ge(DMP)_4$], designed to be highly thermally stable, volatile (see TGA in **Figure 1c**), and reactive, to facilitate low-temperature ALD processing of GeO_2. Using this new liquid, non-pyrophoric, and monomeric precursor (as confirmed by single-crystal XRD and DFT structure analysis in **Figure 1a,b**), we developed a PEALD process for GeO_2 using O_2 plasma as the co-reactant. The process operates across a broad temperature range from 40 °C to 240 °C (**Figure 2a**) with a linear GPC of 0.24 Å at 150 °C. By utilizing different plasma pulse durations (t_{plasma}), the composition of the films can be adjusted: with t_{plasma} = 500 ms, the thin films consist of GeO_2, GeO, and Ge, with a higher degree of sub-stoichiometric GeO_x species at higher deposition temperatures, whereas stochiometric GeO_2 is obtained with t_{plasma} = 50 ms (**Figure 2b, c**). Initial characterization revealed that the composition directly influences the optical behavior of GeO_x thin films, as seen in the UV/Vis spectra of GeO_x thin films deposited using different plasma durations and deposition temperatures (**Figure 3a**). Further, transmission electron spectroscopy revealed closed and uniform thin films with an amorphous structure (**Figure 3b**). Thereby, the rapid nucleation behavior of the process allowed the deposition of a thin film using only eight PEALD cycles. This enabled down-scaling to a film thickness of ≤1 nm (**Figure 3c**), approaching the theoretical thickness required for the bilayer structure and providing a strong foundation to explore the scalable growth and utilization of bilayer GeO_2.

By identifying [$Ge(DMP)_4$] as a new and promising Ge precursor, PEALD processing of GeO_2 and GeO_x becomes feasible at near-room-temperature conditions, advancing the use of GeO_2 and GeO_x thin films for new applications based on their unique properties.

9:00am **AF1-WeM-5 Low Temperature Thermal Atomic Layer Deposition of Bismuth Oxide Thin Films Using a Novel Precursor***, **Taylor Currie**, Patrick Price, Ronald Goeke, Joseph Klesko,* Sandia National Laboratories

Binary, ternary, and multinary bismuth-containing oxide thin films have been synthesized by chemical vapor deposition and atomic layer deposition (ALD), and utilized in optical, ferroelectric, sensing, and catalytic applications. Binary bismuth oxide (Bi_2O_3) exists in several crystalline phases; however, deposition of a targeted single phase, as well as stoichiometric Bi_2O_3, by ALD remains challenging.

A recent study deposited Bi-rich α-Bi_2O_3 on Si(100) substrates by ALD using triphenylbismuth ($BiPh_3$) and ozone (O_3) as precursor and co-reactant, respectively, within an ALD window of 250-300 °C. Alternative substrates or annealing at temperatures between 700 - 800 °C was required to access additional phases (i.e., β and γ) and stoichiometric composition.

Herein, we report a thermal ALD process for Bi_2O_3 using methyldiphenylbismuth ($MePh_2Bi$) and O_3 as novel precursor and co-reactant, respectively. Saturation was achieved with a $MePh_2Bi$ precursor delivery temperature as low as 90 °C, and a growth per cycle of ~ 0.6 Å/cycle within the range of 100 - 170 °C. $MePh_2Bi$, a liquid, methyl-substituted, and thermally stable precursor exhibits higher volatility than its solid $BiPh_3$ analogue, enabling deposition on temperature-sensitive substrates. Characterization by x-ray photoelectron spectroscopy, atomic force microscopy, and grazing incidence x-ray diffraction of the as-deposited films is presented.

9:15am **AF1-WeM-6 Effect of Initial Surface Silanol Density and Aminosilane Structure on O2 Plasma-Assisted ALD of SiO_2***, **Andrew Kaye**,* Colorado School of Mines*; Bhushan Zopé,* Intermolecular, Inc.*; Xinjian Lei, Agnes Derecskei, Ronald Pearlstein, Haripin Haripin Chandra,* EMD Electronics*; Sumit Agarwal,* Colorado School of Mines

SiO_2 is a commonly used dielectric material in semiconductor manufacturing, and aminosilanes are typically used as the Si precursor during radical-assisted atomic layer deposition (ALD) of SiO_2. This work explores the role of the initial surface Si−OH density, the substrate temperature, and the structure of the aminosilane precursor on the growth per cycle (GPC) for ALD on plasma-deposited SiO_2 substrates. Specifically, we studied O_2-plasma-assisted ALD of SiO_2 using two aminosilanes, di-*sec*-butylaminosilane (DSBAS) and dimethylamino trimethylsilane (DMATMS). The surface reactions during ALD were monitored using *in situ* attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy, and the GPC was monitored using *in situ* four-wavelength ellipsometry. On an SiO_2 surface with a high initial Si−OH group density, *in situ* ATR-FTIR spectroscopy shows that ~30% more Si−OH groups are consumed by DMATMS than DSBAS because DSBAS contains a bulkier amino leaving group than DMATMS. *In situ* ellipsometry shows that at an ALD temperature of 100 °C, the GPC using DSBAS and DMATMS are ~1.8 and ~1.2 Å, respectively. The higher GPC for DSBAS shows that the initial aminosilane coverage does not influence the GPC. We speculate that during the O_2 plasma step, O radicals can easily insert into Si−H bonds in adsorbed DSBAS. However, for adsorbed DMATMS, surface Si−$(CH_3)_3$ groups must be combusted, and then converted to Si−OH groups from species generated in the O_2 plasma.

On an SiO_2 surface with a low initial Si−OH group density, approximately the same number of Si−OH groups react with DMATMS and DSBAS. Therefore, we conclude that once the initial surface Si−OH density is sufficiently low, steric effects do not play a role in initial aminosilane adsorption on SiO_2. For both DMATMS and DSBAS, at a constant ALD temperature, the initial SiO_2

surface Si−OH group density has no effect on the GPC of SiO_2 ALD. *In situ* ellipsometry shows that on an SiO_2 surface with a low initial Si−OH group density, no nucleation delay is observed compared to a film with a high initial Si−OH group density. This implies that more Si−OH groups are produced during the first few O_2-plasma half-cycles compared to the initial density of adsorbed aminosilanes on the surface, allowing steady-state ALD to be reached within 5 ALD cycles. As ALD temperature for DSBAS increases, the GPC decreases. This is due to the thermal instability of reactive surface groups such as Si−OH and Si−H, and the areal density of these sites decreases with increasing temperature.

9:30am **AF1-WeM-7 Limits of Plasma Oxidation in Cr_2O_3 Ald: Over-Oxidation, Etching, and Defect Control***, **Soumik Das,*** imec USA*; Huiyun Yang,* University of Michigan, Ann Arbor*; Sean McMitchell,* IMEC Belgium*; Becky (R. L.) Peterson,* University of Michigan, Ann Arbor

Plasma-enhanced atomic layer deposition (PE-ALD) introduces highly reactive oxidation pathways that can fundamentally alter growth mechanisms in multivalent oxides. In p-type Cr_2O_3, plasma exposure does not act as a single monotonic oxidant but instead drives two competing processes: stabilization of Cr^{3+} through efficient ligand removal, and over-oxidation to volatile Cr^{6+} species that induce net etching. In this work, we investigate oxygen plasma-based ALD of Cr_2O_3 using $Cr(acac)_3$, with ozone ALD used only to establish a phase-stable reference growth window. At 250 °C, aggressive plasma dosage conditions suppress net growth, consistent with an etch-dominated regime associated with $Cr^{3+}\rightarrow Cr^{6+}$ conversion and CrO_3 volatilization. Reducing plasma delivery partially restores growth but yields rough, non-uniform films, indicating a transition toward an oxidation-limited regime rather than a conventional ALD window. Atomic force microscopy reveals pronounced surface roughening and poor film uniformity. These results identify stabilization of the Cr^{3+} oxidation state as the central challenge for PE-ALD of Cr_2O_3 and define critical process limits for plasma oxidation in p-type oxide ALD targeting low-temperature electronics.

9:45am **AF1-WeM-8 Composition-Tunable Molybdenum Carbonitride Thin Films Prepared by Plasma-Enhanced Atomic Layer Deposition (PEALD) for Diffusion Barriers in Cu and Ru Interconnects***, **Younjae Shin,*** *Chaehyun Park, Minjeong Kweon, Sang Bok Kim, Soo-Hyun Kim,* Ulsan National Institute of Science and Technology (UNIST), Republic of Korea

Mo-based materials (MoC_x, MoN_x, MoC_xN_y) exhibit high thermal and chemical stability as well as extremely low electrical resistivity. [1] Owing to these superior properties, Mo-based thin films are considered as promising diffusion barrier materials for advanced Cu and Ru interconnects. [2] In MoC_xN_y, C and/or N occupy interstitial sites within the crystal structure, enabling tunable properties. To enable their integration into advanced semiconductor interconnects, MoC_xN_y thin films were deposited by PEALD using a N-free Mo precursor with an H_2+N_2 mixture plasma reactant. By adjusting the H_2:N_2 ratio, the composition of C and N in the MoC_xN_y thin films was systematically controlled. Notably, N incorporation played a decisive role in increasing the growth rate from an extremely low value of 0.3 Å/cycle under pure H_2 plasma to ~1.5 Å/cycle with the introduction of a small amount of N_2, indicating that N_2 promotes surface reactions during MoC_xN_y growth. Under an H_2-rich plasma condition (H_2:N_2 = 8:1), typical ALD behavior was observed, including self-limiting growth with respect to both precursor and reactant pulse times. A stable ALD window was also identified at 225-250 ℃, within which a saturated growth rate of ~1.5 Å/cycle and linear thickness evolution with the number of cycles were achieved. Moreover, both the growth rate (1.5-1.9 Å/cycle) and electrical resistivity (590-1490 μΩ·cm) were effectively tuned by varying the H_2:N_2 ratio from 8:1 to 1:8. Structural and compositional analyses using XRD and XPS confirmed the formation of conductive MoC_xN_y thin films with controlled C and N incorporation. Electrical characterization also revealed a strong correlation between film composition and resistivity. Finally, the PEALD-MoC_xN_y thin films were applied as diffusion barrier for Cu and Ru interconnects as well as gate electrode and the results will be presented at the conference.

References

[1] Kang, W. et al. *Journal of Vacuum Science & Technology a Vacuum Surfaces and Films* (2023): *41* (6).

[2] Tripathi, C. C et al. *Applied Surface Science* (2008): *255* (6), 3518–3522.

Acknowledgements

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ALD Fundamentals: Growth and Characterization
Room HB Plant Ballroom - Session AF2-WeM

Plasma-enhanced ALD of Nitrides

Moderators: Andrew Cavanagh, University of Colorado at Boulder, **Craig Huffman**, Oxford Instruments

10:45am **AF2-WeM-12 Low-Temperature Plasma-Enhanced Atomic Layer Deposition of Crystalline Gan Thin Films Using Monovalent Organogallium Precursor***, **Fumikazu Mizutani,*** *Nobutaka Takahashi,* Kojundo Chemical Laboratory Co., Ltd., Japan

GaN thin films are promising wide-gap semiconductors, and the low-temperature atomic layer deposition (ALD) of high-quality crystalline GaN films is being actively investigated. In ALD of GaN, trimethylgallium (TMG; $Ga(CH_3)_3$), triethylgallium (TEG; $Ga(C_2H_5)_3$) are widely used. However, there have been almost no reports on obtaining high-purity crystalline GaN films at temperatures below 350 °C.

We have developed a novel liquid precursor (GaCp*; pentamethylcyclopentadienyl gallium) for the ALD of high-purity Ga_2O_3 films [1]. A film with almost no impurities was obtained using ABC-type ALD at a low temperature of 200 °C consisting of precursor adsorption, ligand elimination, and surface oxidation processes. Here, we report the results of investigating a similar ABC-type ALD process to obtain high-purity crystalline GaN at 200 °C.

GaN films were deposited at 200 °C on 150 mm Si wafers with native oxide films using a FlexAL system (Oxford Instruments) with a remote plasma generator and an in situ spectroscopic ellipsometer. In one ALD cycle, GaCp* was used as a precursor, and H_2 plasma followed by N_2 plasma was used as the reactant. In this process, the aromatic anion ligand Cp* was desorbed by H_2 plasma, and the surface Ga was nitrided by N_2 plasma.

Self-limiting reactions were observed for GaCp*, H_2 plasma, and N_2 plasma pulse times of 0.5, 20, and 20 s, respectively. Next, we measured the GPC of ALD using the pulse times. The relationship between the number of ALD cycles and film thickness was linear, with a GPC of 0.023 nm/cycle. The sample, which was deposited in 600 cycles and had a film thickness of approximately 14 nm, was subjected to impurity analysis by GDOES and observation of crystallinity by cross-sectional TEM.

GDOES analysis showed that almost no C impurities were detected, suggesting that the ligands were sufficiently removed by H_2 plasma. Clear lattice fringes were observed in the cross-sectional TEM image, indicating that the GaN thin film was highly crystalline. In this study, deposition was performed on a native oxide film of silicon, but it is expected that epitaxial films can be deposited on templates such as sapphire.

The reason why high-purity, highly crystalline GaN could be deposited even at a low temperature of 200 °C is thought to be because GaCp* is a monovalent precursor, meaning that monovalent GaCp* is more advantageous for ligand elimination than trivalent TMG and TEG.

Reference[1] F. Mizutani, S. Higashi, M. Inoue, and T. Nabatame, J. Vac. Sci. Technol. A 38, 022412 (2020).

11:00am **AF2-WeM-13 Plasma-Enhanced Growth of Low-κ Amorphous Boron Nitride: From 25 °C to 400 °C***, **Daehyun Ko,*** *Fu-Chun Sheu, Luwen Li, Xun Zhan,* UT Austin*; John Carroll, Sergio Gamez-Puente, Hu Li, Peter Ventzek, Jianping Zhao,* Tokyo Electron America*; John Ekerdt, Jamie Warner,* UT Austin

The International Roadmap for Devices and Systems (IRDS) highlights the critical need for new dielectric materials that reduce permittivity and meet reliability requirements for future interconnect architectures. As interconnect dimensions scale into the sub-25 nm regime, conventional silicon-based dielectrics face significant challenges in mitigating parasitic capacitance and crosstalk while satisfying the rigorous mechanical and barrier requirements for integration. Amorphous boron nitride (a-BN) has emerged as a promising alternative for these applications because it offers

a unique combination of low permittivity, high mechanical strength, and excellent chemical stability.

In this work, we demonstrate the plasma-enhanced growth (100 MHz capacitively coupled plasma) of a-BN onSiO_2/Si(001) using borazine ($B_3N_3H_6$) as a single-source precursor. We explore a wide processing window, ranging from room temperature (25 °C) to 400 °C. Growth is governed by weak, reversible physical adsorption and plasma exposure time. During a growth cycle, borazine is adsorbed on the substrate, the chamber is purged/evacuated, and an Ar plasma is ignited. The plasma activates the adsorbed borazine by dissociating the B-H and N-H bonds and breaking open the ring structure. *In situ* X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FTIR) analyses confirm the formation of stoichiometric, sp^2-bonded films with exceptional purity (<1 at.% carbon) and no resolvable B-C or B-O bonding features over a 25 to 400 °C window. By rigorously defining the thickness of a-BN (~14 nm) grown at 25 °C via cross-sectional scanning transmission electron microscopy (STEM) and electron energy loss spectroscopy (EELS) of the fabricated metal-insulator-metal (Au/a-BN/SiO_2/Si) capacitors, we extracted a dielectric constant of ~2.94, validating the potential of a-BN for back-end-of-line integration.

We further investigated the temperature dependence of film properties by extending the growth window from 100 °C to 400 °C. Although Fast Fourier transform (FFT) analysis confirms the emergence of short-range lamellar ordering at elevated temperatures, transmission electron microscopy (TEM) and EELS confirm the preservation of a global amorphous phase and an sp^2-bonded network throughout this transition. Consistent with this, X-ray reflectivity (XRR) reveals a linear increase in film density with temperature, reaching ~2.10 g cm^{-3} at 400 °C. This densification correlates with enhanced environmental stability, offering a tunable pathway to synthesize high-quality a-BN dielectrics optimized for diverse thermal budgets.

11:15am **AF2-WeM-14 Comparing the Effect of H_2 and N_2 Plasma on Boron Nitride Surface During Plasma Enhanced Atomic Layer Deposition Using Density Functional Theory**, ***Tsung-Hsuan Yang***, *Jianping Zhao, Peter Ventzek,* Tokyo Electron America

Boron nitride (BN) has emerged as a promising candidate for next–generation semiconductor and dielectric materials due to its wide bandgap, chemical stability, and compatibility with advanced device architectures. However, the intrinsic inertness of BN surfaces presents challenges for thin–film growth and surface functionalization, particularly when using conventional precursors such as boron trichloride (BCl_3) or borazine ($B_3N_3H_6$), which exhibit limited surface reactivity. Plasma-assisted processes employing hydrogen (H_2) or nitrogen (N_2) are therefore commonly used to activate BN surfaces, although the underlying reaction mechanisms remain poorly understood.

In this work, density functional theory (DFT) calculations are used to investigate the reaction mechanisms and energetics of H_2 and N_2 plasma interactions with boron nitride surfaces. Plasma environments are modeled using atomic hydrogen and nitrogen radicals to represent the highly reactive plasma species. Adsorption configurations, reaction pathways, and activation barriers are analyzed to elucidate key differences between hydrogen- and nitrogen-based plasma treatments.

Our results show that hydrogen radicals preferentially interact with surface nitrogen sites, leading to hydrogen termination and, in some cases, B–N bond dissociation. In contrast, nitrogen radicals promote nitrogen incorporation and surface restructuring through B–N bond formation and the generation of N_2-like dimer species. These distinct reaction pathways produce markedly different surface chemistries, which influence subsequent precursor adsorption and thin–film growth behavior. Based on the calculated energetics, we identify process conditions under which plasma species can selectively tailor surface reactivity, enabling control over film geometry, stoichiometry, and structural evolution.

11:30am **AF2-WeM-15 Precise and Narrow Ion-Energy Distributions in Plasma-Enhanced ALD of Nitrides Using Tailored-Waveform Biasing**, *Arthur de Jong, Silke Peeters, Harm Knoops, Erwin Kessels,* ***Adrie Mackus***, Eindhoven University of Technology, Netherlands

Plasma-enhanced ALD (PEALD) is a powerful approach for the low-temperature growth of nitride thin films, where controlled ion bombardment can be used to tailor film composition, density, and functional properties. In previous work, we have demonstrated that radiofrequency (RF, 13.56 MHz) substrate biasing provides beneficial ion-energy effects during PEALD, enabling improved electrical and structural properties of a range of dielectrics and conductive nitrides [1,2]. However, the achievable process window can benefit from more precise, narrow, and independent control over the ion energy.

In this contribution, we demonstrate tailored-waveform (TW) substrate biasing at 200 kHz as an advanced ion-energy control scheme [3] for PEALD, offering narrow and well-defined ion-flux energy distribution functions (IFEDFs) without increasing the plasma density [4]. We apply this approach to the PEALD of several technologically-relevant metal nitrides, including AlN_x, TaC_xN_{1-x}, TiN_x, and NbN_x, using Ar–N_2–H_2 plasma mixtures.

By systematically tuning the ion energy via TW biasing, clear and material-specific structure–property relationships are observed. For AlN_x, an increased refractive index and reduced oxygen incorporation are achieved, while for conductive nitrides (TaC_xN_{1-x}, TiN_x, and NbN_x) significant reductions in electrical resistivity are obtained. These results are consistent with, and extend beyond, earlier RF-bias PEALD studies, highlighting the role of controlled low-energy ion bombardment in densification, impurity suppression, and microstructural optimization.

Overall, tailored-waveform biasing provides substantially narrower and better-defined ion-energy distributions, transforming ion energy during ALD into a high-precision knob for materials design.

This work was carried out in collaboration with Oxford Instruments and Prodrive Technologies. An Oxford Instruments FlexAL ALD reactor in the TU/e NanoLab was retrofitted with a Prodrive Technologies prototype low-frequency tailored waveform generator.

[1] T. Faraz *et al*., *Tuning material properties of oxides and nitrides by substrate biasing during plasma-enhanced atomic layer deposition*, ACS App. Mater. Interfaces 10, 13158 (2018).

[2] S. A. Peeters *et al*., Ultrathin superconducting TaC_xN_{1-x} films prepared by plasma-enhanced atomic layer deposition with ion-energy control., App. Phys. Lett. 123, 132603 (2023).

[3] T. Faraz et al., *Precise ion energy control with tailored waveform biasing for atomic scale processing*, J. Appl. Phys. 128, 213301 (2020).

[4] T. Faraz *et al*., *Tailored waveform biasing in atomic and molecular plasmas for atomic-scale processing*, submitted.

11:45am **AF2-WeM-16 Characterizing Inductively Coupled Plasmas in Ar/N_2/H_2 Mixtures for Plasma Enhanced Atomic Layer Deposition**, ***David Boris***, *Jeffrey Woodward, Virginia Wheeler, Michael Johnson, Mackenzie Meyer, Scott Walton,* U.S. Naval Research Laboratory

Low temperature plasmas containing mixtures of Argon, Nitrogen, and Hydrogen are widely used in the plasma enhanced atomic layer deposition of crystalline metal nitrides (e.g. AlN) at low temperatures (<500C) [1,2,3].Generally, the addition of H_2 is beneficial in that it facilitates the removal of precursor ligands and leads to films with low carbon content (<1%). In addition, if the process conditions are properly chosen, highly crystalline metal-nitride films can be grown in Ar/N_2/H_2 mixtures.However, the effects of H_2 addition on the downstream plasma properties near the substrate are not well understood in remote, inductively coupled plasma (ICP) geometries.As such, a better understanding of the downstream plasma properties in this gas chemistry will be the focus of this presentation.

In this work, we use a combination of Langmuir probes, a retarding field energy analyzer, and optical emission spectroscopy (OES) to examine the effects of varying process parameters on the physical characteristics of Ar/N_2/H_2 plasmas generated in a remote, ICP geometry.In particular, a range of applied RF powers, gas flows, and pressures are explored with a focus on the resulting changes in atomic species density, plasma density, plasma potential, and the energy and flux of ions at the substrate.Of particular interest is the effect H_2 has on the ion flux and ion energy distribution at the substrate. These changes in plasma properties are then tied to changes in the characteristics of AlN thin films grown via plasma-enhanced ALD using a remote ICP employing Ar/N_2/H_2 gas mixtures. This work was supported by the NRL Base program through the Office of Naval Research.

[1] N. Nepal, et al Appl. Phys. Lett. 103, 082110 (2013)

[2] M. J. Sowa, et al J. Vac. Sci. Technol. A 34, 051516 (2016)

[3] M. F. J. Vos, et al J. Phys. Chem 122, 39 (2018)

Area Selective ALD
Room Tampa Bay Salons 3-4 - Session AS1-WeM

ASD Process I

Moderators: Sumit Agarwal, Colorado School of Mines, **Stacey Bent**, Stanford University

8:00am **AS1-WeM-1 ALD Outstanding Presentation Award Finalist: Triazolylidene Small Molecule Inhibitor for Area-Selective Atomic Layer Deposition of High *k*-Dielectric Materials**, *Giang Hoang Pham,* Western University, Canada*; Jordan Bentely,* Wesleyan University, Canada*; Dana Nanan, Cathleen Crudden,* Queen's University, Canada*; **Paul Ragogna**,* Western University, Canada

High selectivity in area selective atomic layer deposition (AS-ALD) requires the effective performance of an inhibitor that must exhibit selectively binding mode on non-growth areas as well as strong thermal, and chemical stability to prevent degradation or decomposition during the semiconductor manufacturing process. N-heterocyclic carbenes (NHCs) have emerged as promising next-generation alternatives to conventional small-molecule inhibitors (SMIs) due to their strong *σ*-donor character and preferential binding to metal surfaces over a dielectric region. We have prepared and developed *triazolylidene* NHC (Tz) derivatives as a novel class of NHC inhibitor for selective high-k dielectric growth on SiO_2 over metallic bands reaching a selectivity factor of 93% after 50 dielectric deposition cycles. The selective adsorption behavior and dielectric blocking efficiency were systematically evaluated using time-of-flight secondary ion mass spectrometry (ToF-SIMS), and X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM). The practical applicability of the Tz inhibitor is further demonstrated through bottom-up fabrication of a working field-effect transistor, in which the NHC selectively protects metal electrodes during the deposition of metal oxide dielectric and semiconductor layers. This work paves an innovative pathway for exploring novel class of SMIs toward advanced AS-ALD applications.

Selected references: (1) D.A.R. Nanan, J.T. Lomax, J. Bentley, L. Misener, A.J. Veinot, W-T Shiu, L. Liu, P.J. Ragogna**,** C.M. Crudden *J. Am. Chem. Soc.***2025**, *147*, 5624–5631; **(2)**J.T. Lomax, E. Goodwin, M.D. Aloisio, A.J. Veinot, I. Singh, W-T Shiu, M. Bakiro, J. Bentley, J.F. DeJesus, P.G. Gordon, L. Liu, S.T. Barry, C.M. Crudden, P.J. Ragogna *Chem. Mater.***2024**, *36*, 5500–5507; **(3)** P.J. Ragogna, C.M. Crudden, D.A.R. Nanan, J.T. Lomax, A.J. Veinot, J. Bentley, "Method of Selective Deposition of Triazolylidenes on Metallic Surfaces", International Patent Application No. PCT/CA2025/051508, filed: Nov. 12, 2025

8:30am **AS1-WeM-3 Maintaining Healthy Boundaries – Machine Learning Design of SMIs**, ***Sean Barry***, *Marshall Atherton,* Carleton University, Canada*; Dennis Hausmann, Jiyeon Kim,* Lam Research Corp.

Machine learning–guided molecular design is important for accelerating materials discovery, and we have applied it to area-selective atomic layer deposition (AS-ALD). In this work, we integrate machine learning with systematic experimental characterization to guide the development of amino-substituted silane small-molecule inhibitors (SMIs) to optimize volatility, thermal stability, and surface selectivity. By prioritizing data-driven structure–property relationships, this study helps establish a predictive framework for identifying viable SMIs while limiting experimental trial-and-error.

A diverse library of aminosilanes was synthesized using an environmentally benign nucleophilic substitution route involving disubstituted amines and chlorosilanes, with triethylamine as a sacrificial base. This approach avoids pyrophoric reagents and metal-containing intermediates, supporting sustainable scale-up. Thermal properties were evaluated using thermogravimetric analysis, vapour pressure measurements, and differential scanning calorimetry. Surface adsorption and selectivity were quantified using in situ quartz crystal microbalance measurements.

The experimentally derived thermophysical dataset was used to train ML models to map molecular structure and composition to key properties governing AS-ALD performance, including volatility and thermal stability. A chemistry-informed molecular property prediction platform (DeepAutoQSAR, Schrödinger) helped identify optimal model architectures. The resulting ML models were used to predict properties of previously untested silane precursors, enabling targeted selection of candidates for experimental validation. Comparison of predicted and measured properties demonstrates the effectiveness of this ML-guided workflow for accelerating inhibitor design.

8:45am **AS1-WeM-4 Role of Precursor and Aklanethiol Chain Length on Area Selective Deposition of Aluminum and Hafnium-Containing Films**, ***Nicholas Strandwitz***, Lehigh University

Area selective atomic layer deposition (AS-ALD) enables the selective placement of material based on differences in surface chemistry and is thus a promising strategy for device manufacturing by avoiding addition patterning steps and alignment issues.Key developments that are being sought include achieving high selectivity (near 100%) at high film thicknesses on growth surfaces, and expanding the palette of materials (such as new low-k materials) that can be grow in AS-ALD.In this talk I will explore two aspects of our work that work toward these developments: Examination of the role of alkanethiol chain length and examination of the role of alternative metal and co-reactant precursors on selectivity.

The stability and impermeability of monolayer-based blocking layers is critical to preventing film growth in certain regions.Few reports explicitly studied the effect of alkane chain length and temperature on selectivity, so we sought to do so with a series of alkanethiols of various alkane chain length on copper surfaces.We found that longer chain lengths achieved higher selectivity and all chain lengths to be unstable to the highest temperature investigated (180 °C).To isolate the precise breakdown mechanisms, we separately subjected the alkanethiol monolayers on copper to various individual ALD steps including elevated temperature, metal precursor exposure, or water exposure.We found that trimethylaluminum at elevated temperature induced alkanethiol desorption, whereas amido-based Hf precursors did not, thus demonstrating a chemical effect on monolayer stability.

To further investigate the role of film precursor, we studied an array of metal and non-metal precursors including alkyl aluminums, amido aluminum, aluminum alkoxide, and ethylene glycol.Importantly, we found that precursor size, rather than reactivity, was the prime determining factor in realizing high sensitivity.We found that molecular layer deposited films (using ethylene glycol) did not show significantly higher selectivity than traditional ALD growths with the same metal precursor.With certain combinations of large metal precursors and water, we were able to achieve high selectivity (>90%)at alumina film thicknesses greater than 15 nm on the growth surface.Thus, this work builds on existing reports from other groups that the precursor chemistry has a massive role in determining selectivity.

9:00am **AS1-WeM-5 Surface Blocking Effect of NH_3 in Selective Co-ALD with CCTBA Precursor**, ***Naoki Tamaoki***, *Jun Yamaguchi, Noboru Sato, Atsuhiro Tsukune, Yukihiro Shimogaki,* The University of Tokyo, Japan

As semiconductor devices continue to scale down, current densities in interconnects increase, leading to serious reliability degradation of Cu interconnects due to electromigration. The introduction of a metallic Co cap layer is expected to enhance adhesion between interconnects and dielectric layers, thereby extending the lifetime of Cu wiring. In Co atomic layer deposition (ALD) using CCTBA (Cobalt Carbonyl Tertiary-Butyl Acetylene) as a precursor, an incubation period exists in which film nucleation on SiO_2 dielectric surfaces is delayed compared with Cu surfaces, enabling selective growth [1]. In this study, the inhibitor effect of NH_3 was evaluated as a method to further enhance selectivity, motivated by previous reports on selective CVD using $Co_2(CO)_8$, where simultaneous NH_3 supply suppresses growth initiation and improves selectivity [2].

Deposition experiments were performed on Si substrates with a 300 nm thermally grown oxide layer at 120 °C using alternating CCTBA and H_2 pulses for 500 cycles, with in-situ monitoring by spectroscopic ellipsometry. Under standard conditions, no incubation period was observed and a growth-per-cycle (GPC) of 0.016 nm/cycle was obtained. When NH_3 was co-supplied during the CCTBA pulse, an incubation period of approximately 75 cycles appeared and the GPC decreased to 0.0099 nm/cycle, demonstrating that NH_3 functions effectively as an inhibitor.

Furthermore, surface reaction calculations using a machine-learning potential (PFP: Preferred Potential by Matlantis Corp.) suggest that NH_3 selectively adsorbs on OH groups on oxide surfaces, which serve as potential adsorption sites for CCTBA molecules, thereby blocking these reactive sites. These results indicate that NH_3 can act as a small-molecule inhibitor in Co-ALD using CCTBA, providing a promising approach for enhancing selective growth in Co capping processes for advanced interconnect applications.

The authors gratefully acknowledge Daikin Industries, Ltd. For their support and valuable discussions.

References

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[2] Z. V. Zhang et al., J. Vac. Sci. Technol. A 38, 033401 (2020).

9:15am **AS1-WeM-6 Fluorination Passivation for Area-Selective Deposition: Selective Passivation of SiO_2 vs SiN_x for Highly Selective TiO_2 Deposition using Water-Free $TiCl_4/Ti(^iPrO)_4$.**, ***Jeremy Thelven***, *Gregory Parsons,* North Carolina State University

There is an acute need for new memory and computing device structures that are more energy efficient.[1] To minimize energy loss, new complex 3D architectures are needed with precisely aligned features. To address inherent alignment limitations in lithographic patterning, area selective deposition (ASD) is an attractive process because, in principle, the alignment between the starting pattern and the deposited feature is determined by differences in reactivity for the molecules on the desired growth and non-growth surfaces. Therefore, when the growth and non-growth surfaces have similar active surfaces sites, such as SiO_2 and SiN_x, identifying reactants that preferentially deposit on one surface versus another is particularly challenging. Recently, we found that when a patterned SiO_2/SiN_x surface was exposed to a fluorinating agent (such as MoF_6), the SiO_2 surface became preferentially passivated for deposition of TiO_2 ALD using $TiCl_4/H_2O$, allowing selectivity >93% for ~9.6 nm of TiO_2.[2] We hypothesized that as ALD proceeds, a primary reason for the observed loss of SiO_2 passivation was unwanted oxidation during the water exposure step.

To address this, we reconsidered a previously studied "waterless" TiO_2 ALD process using $TiCl_4$ and titanium isopropoxide (TTiP) at 210℃.[3] Using $TiCl_4$/TTiP ALD on blanket SiO_2 and SiN_x substrates, we found (Figure 1a and b) that after pre-treating the SiO_2 and SiN_x with only a brief dip in dilute $HF_{(aq)}$, the $TiCl_4$/TTiP process showed delayed deposition on both surfaces. However, the extent of delay was much more substantial on the SiO_2 vs SiN_x, allowing several nm of ASD. Subsequently, we tested the same SiO_2/SiN_x surfaces after dilute $HF_{(aq)}$ followed by exposure to MoF_6 for 1 second at 210℃. As shown in Figure 1c and d, initial results indicate substantially improved selectivity for the fluorine-passivated water-free TiO_2 ALD, enabling ~ 25 nm of TiO_2 on SiN_x vs. SiO_2 with exceptionally high selectivity. The lines in the figures correspond to fits obtained from an analytical nucleation model.[4] Confirmation of these findings will require testing the process on nanoscale patterned substrates. Overall, these results demonstrate how the combination of pretreatment and precursor selection can help achieve chemical contrast for ASD, even on starting surfaces with similar chemical structure and composition.

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2.Thelven, J. M.; Parsons, G. N. et al., Adv Materials Technologies 2025, 10 (23), e00284.
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4.Parsons, G. N. JVSTA 2019, 37 (2), 020911.

9:30am **AS1-WeM-7 Chemical Selectivity in Atomic Layer Selectivity (ALD) via Gas-Phase Silylation using N-(trimethylsilyl)dimethylamine (TMSDMA)**, *Mohammed Sadam Alam,* ***Francisco Zaera***, University of California at Riverside

The effectiveness of the silylation of both silicon oxide and copper surfaces using N-(trimethylsilyl)dimethylamine (TMSDMA) as a passivation agent in atomic layer depositions (ALDs) was evaluated and contrasted by using x-ray photoelectron spectroscopy (XPS). It was determined that on SiO_2 such silylation does indeed block the nucleation centers where the ALD precursors are activated and therefore inhibit film growth, but only temporarily; after a few ALD cycles, deposition becomes evident. By testing this chemistry on two types of SiO_2 surfaces, prepared by plasma-enhanced chemical vapor deposition (PE-CVD) and by chemical (RCA) treatment of Si(100) wafers, it was concluded that the nature of the initial substrate does not play a crucial role in the silylation or ALD blocking processes. The material being deposited, on the other hand, does make a difference: TiO_2 film growth can be blocked for almost 10 ALD cycles, whereas HfO_2 starts building up on the surface after less than 5 ALD cycles. Moreover, the steady-state deposition rate for TiO_2 was determined to be lower than for HfO_2. One of the key findings of this work is that the silylation can be carried out using either gas- or liquid-phase treatments. It was found that the extent of silylation and the inhibition of the subsequent ALD were comparable in both cases, but the gas-phase method was determined to be cleaner and to deposit less carbon contaminants.

On copper, by contrast, virtually no effect on the ALD of either TiO_2 or HfO_2 was observed upon silylation with TMSDMA. A slow but detectable initial rate of oxide deposition was observed either before or after treatment, similar in both cases: approximately 0.15 Å/cycle in the case of TiO_2, about 0.25 Å/cycle for HfO_2. On SiO_2, by contrast, these rates were measured to be ~0.6 and 1.2 Å/cycle, respectively, on the clean substrate, but only ~0.08 and 0.4 Å/cycle after silylation. Consequently, it is concluded that gas-phase silylation using TMSDMA can be used to selectively allow for the ALD of oxides on silica in the presence of copper, that is, for area-selective ALD (AS-ALD), albeit with limited contrast. It should be added that in some cases an induction period was observed before the start of the film growth. We speculate that this, and the non-zero deposition rates seen on Cu and silylated SiO_2, may be due to the possible existence of defects on the substrates acting as nucleation centers.

9:45am **AS1-WeM-8 Mechanistic Criteria for Area Selective Deposition of Multicomponent Al_xSi_yO Oxide Dielectrics**, *Eryan Gu, Zilian Qi, Kun Cao,* ***Rong Chen***, Huazhong University of Science and Technology, China

As integrated circuit technology continues to evolve towards three-dimensional architectures, device density and interconnect layers are constantly increasing. Area selective deposition (ASD) offers significant advantages as a bottom-up approach for such patterning. In this talk, an ASD process and selectivity criterion for multicomponent oxide of AlxSiyO is presented. Combined experimental and mechanistic analysis, the interactions between Al and Si precursors and their interactions with inhibitor modified surfaces were revealed. A selectivity criterion driven by penetration depth of precursors into inhibitors and the reaction barrier of multiple precursors was established, enabling selective deposition through precursor selection and composition regulation. The growth of AlxSiyO films is controlled by the synergistic effect of catalytic activation, precursor ratio and temperature, and has tunable dielectric properties, which is expected to improve the RC delay problem. Inhibition of ligand elimination at low temperatures leads to moderate carbon incorporation, thereby enabling the film dielectric constant to reach 4.3. Highly selective growth of 10 nm AlxSiyO films was achieved on Cu/SiO2 patterned, demonstrating a viable strategy for integrating AlxSiyO into next-generation interconnect technologies.

Area Selective ALD
Room Tampa Bay Salons 3-4 - Session AS2-WeM
ASD Process II

Moderators: Anjana Devi, Leibniz Institute, IFW Dresden, **Nicholas Strandwitz**, Lehigh University

10:45am **AS2-WeM-12 Perfect Selectivity vs Practical Sustainability in ASD**, ***Nupur Bihari***, Lam Research Corporation **INVITED**

Area selective deposition (ASD) continues to emerge as a pivotal technique for enabling next–generation semiconductor manufacturing, particularly as device geometries shrink and integration demands intensify. However, the long–standing goal of achieving perfectly selective growth often drives processes toward excessive complexity, high precursor consumption, and limited long–term sustainability. In this work, we explore the practical balance between achieving robust selectivity and maintaining overall process efficiency, emphasizing the potential benefits of reducing chemical usage without compromising integration–relevant performance. By adopting a more pragmatic viewpoint, we demonstrate that high–quality selectivity does not necessarily require aggressive surface treatments, extreme exposure times, or high precursor flows. Instead, a carefully tuned, eco–friendly process regime can deliver excellent material discrimination while significantly lowering chemical burden and overall environmental impact.

To evaluate performance under these more sustainable conditions, we employ top–down scanning electron microscopy (TDSEM) as a straightforward yet powerful metrology approach. TDSEM enables rapid assessment of nucleation behavior, feature–scale uniformity, and pattern fidelity, providing a clear window into the relationship between precursor flow, growth onset, and ultimate selectivity. Our results show that excellent selectivity can still be reliably achieved even when precursor usage is dramatically reduced, illustrating the feasibility of simplifying ASD processes for manufacturing–scale deployment. Electrical resistance–capacitance (RC) measurements and integrated wafer–level data further confirm that processes exhibiting modest deviations from perfect selectivity can nonetheless support high–performance interconnect scaling and patterning fidelity. These findings challenge the traditional assumption that optimal integration requires flawless selectivity and instead suggest that controlled,

minimal nucleation on non–growth surfaces may be tolerable - especially when weighed against the benefits of lower cost, reduced chemical waste, and substantially improved throughput.

Taken together, this work highlights the value of shifting from a perfection–driven mindset to a more holistic framework that prioritizes precursor efficiency, environmental responsibility, and integration robustness. By demonstrating that sustainable, lower–chemistry ASD regimes can still meet stringent device requirements, we outline a more realistic and scalable pathway for adopting ASD in high–volume semiconductor manufacturing. This approach not only reduces overall process strain but also strengthens the connection between small–scale laboratory studies and real–world wafer–level performance, ultimately enabling faster development cycles and broader implementation of ASD–driven patterning strategies.

11:15am **AS2-WeM-14 Photoassisted Chemical Vapor Deposition as a Strategy for Area Selective Deposition of Ru:Implications for Developing an ALD Process**, *Christopher Brewer,* University of Texas at Dallas*; Rashmi Singh,* Unversity of Florida*; James Pugh, Anjali Sharma,* University of Florida*; Amy Walker,* University of Texas at Dallas*;* ***Lisa McElwee-White****,* University of Florida

Photoassisted chemical vapor deposition (PACVD) is a potentially attractive technique for metallization of thermally sensitive substrates. Prior PACVD results from (η^3-allyl)$Ru(CO)_3Br$, $CpRu(CO)_2Me$, and $(COT)Ru(CO)_3$ have demonstrated that allyl and Cp ligands remain incorporated in deposits, while the COT ligand was not detected. Subsequently, a library of (η^4-diene)$Ru(CO)_3$ and (η^2-alkene)$Ru(CO)_4$ precursors that undergo photochemical ligand loss at room temperature has been prepared and their solution photochemistry studied. 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-alkene)$Ru(CO)_4$ 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. The deposition results will be discussed in context of precursor design for ASD and development of related ALD processes.

11:30am **AS2-WeM-15 Highly Selective Ru Growth on Metallic Substrates against Dielectric Surface via Inherent Area-selective Atomic Layer Deposition Using a Novel Ru Precursor**, ***Hideaki Nakatsubo****, Masato Iseki,* TANAKA PRECIOUS METAL TECHNOLOGIES Co., Ltd., Japan*; Shintaro Chiba,* EEJA Ltd., Japan*; Iaan Cho, Hyungjun Kim,* Yonsei University, Republic of Korea*; Bonggeun Shong,* Hanyang University, Republic of Korea*; Debananda Mohapatra, Jeongha Kim, Soo-Hyun Kim,* UNIST, Republic of Korea

Area-selective deposition via atomic layer deposition (AS-ALD) offers a bottom-up approach to fabricate complex and functional nanostructures, being robust for the scaled architectures even with any 3D structures compared to the conventional top-down approach using multi-patterning processes. Inherent-type AS-ALD is the most simplified process, exploiting intrinsic adsorption properties of the precursors depending on the substrates. Compared to inhibitor-assisted area-selective processes, the inherent AS-ALD also highlights practical advantages such as reducing fabrication steps or eliminating concerns of residual inhibitors, which is attractive for the application of interconnect metallization.

Although the inherent AS-ALD has typically suffered from a lower selectivity compared to that of inhibitor-assisted one, a higher inherent selectivity against Si-based dielectrics such as SiO_2, low-k or SiN is essential for the intended purposes (e.g., void-free/seamless bottom-up metallization). Therefore, we demonstrated high selectivity against SiO_2 via Ru thermal AS-ALD using a novel Ru precursor, [Ru(TMM)(*p*-cymene)], and O_2 as a reactant without any inhibitor or other area-selective activation methods. This precursor has two different ligands, trimethylenemethane (TMM) and isopropylmethylbenzene (*p*-cymene), and exhibits high thermal stability (> 400 ^oC). A previous report on this precursor revealed that a surprisingly long incubation period of >1000 cycles was observed on SiO_2 while only ~8 cycles were required on TiN at 300 ^oC [1], overcoming the challenges of high selectivity which previous Ru AS-ALDs have suffered from. Computational simulations in the same report also discovered that dissociative adsorption proceeds on metallic substrates such as Ru, but is energetically unfavorable on SiO_2, providing the theoretical support for the high inherent selectivity against SiO_2.

In this study, we expand our understanding of the inherent AS-ALD Ru on technologically important metallic substrates including Ru, TiN, Mo, W against dielectric substrates such as SiO_2, low-k, SiN, Al_2O_3. The results demonstrate that the high selectivity against dielectrics was confirmed both on blanket wafers and patterned substrates. We also discuss how process conditions affect the selectivity and the experimental factors required to emerge the selectivity with mechanistic insights.

[1] H. Nakatsubo *et.al*., *Adv. Sci*., **2025**, e19209.

11:45am **AS2-WeM-16 Mechanistic Insights into Area-Selective Etching of Ruthenium** *,* ***Iaan Cho****,* Yonsei University, Republic of Korea*; Soo-Hyun Kim,* Ulsan National Institute of Science and Technology, Republic of Korea*; Hyungjun Kim,* Yonsei University, Republic of Korea*; Bonggeun Shong,* Hanyang University, Republic of Korea

As interconnect linewidths continue to scale down, ruthenium (Ru) is being considered as an alternative to copper (Cu) owing to its favorable resistivity and reliability at reduced dimensions. For practical integration, area-selective deposition (ASD) is suggested as an alternative fabrication method to confine Ru growth to conductive growth regions while suppressing deposition on dielectric non-growth areas (NGAs) [1]. However, since nucleation of Ru on the NGAs such as SiO_2 can limit the applicability of the process, addition of oxidative etch-back steps within ASD are suggested to enhance the overall deposition selectivity [2]. In this study, the mechanistic origin of the selectivity in oxidative etching of Ru was investigated using machine-learning interatomic potential (MLIP) based energetic analyses and molecular dynamics (MD) simulations. Several different environments of Ru nuclei on metallic and dielectric substrates, such as Ru adatoms, sub-nanometer clusters, and extended heterointerfaces are considered. The results indicate that Ru species on dielectric surfaces are readily oxidized and desorb as volatile RuO_4 upon exposure to oxidant such as O_3, whereas Ru on metallic surfaces are less susceptible to oxidative loss under comparable conditions. This substrate-dependent reactivity upon oxidation and desorption is consistent with experimentally reported selectivity enhancements in the supercycle ASD processes. These results clarify the selective oxidative etching of Ru and provide a mechanistic basis for optimizing Ru ASD for advanced interconnect integration. Acknowledgments. This work was supported by the Technology Innovation Program [Public-Private Joint Investment Semiconductor R&D Program (K-CHIPS) To Foster High-Quality Human Resources] [RS-2023-00236667, High Performance Ru-Tin Interconnects Via High Temperature Atomic Layer Deposition (ALD) and Development on New Interconnect Materials Based on ALD] funded by the Ministry of Trade, Industry & Energy (MOTIE, Korea) (No. 1415187401).References. [1] Chem. Mater. 2024, 36, 18, 8663; [2] Chem. Mater. 2019, 31, 11, 3878

Emerging Materials and Processes
Room Tampa Bay Salons 1-2 - Session EM1-WeM
Conductive ALD Films

Moderators: Jean-François de Marneffe, IMEC, **Henrik Sønsteby**, University of Oslo

8:00am **EM1-WeM-1 Platinum Growth on Li-Based Thin Films Using Thermal ALD**, ***Manon LETICHE****, Sylvain POULET, Nicolas MASSONI, Violaine SALVADOR, Hélène COURDERT-ALTEIRAC, Nicolas GAUTHIER, Messaoud BEDJAOUI,* CEA-LETI, France

Lithium-based layers are key players in developing nanostructured energy storage systems. As such, ultrathin lithium phosphorous oxynitride LiPON deposited by Atomic Layers Deposition (ALD) is incorporated as solid-electrolyte between two electrodes for on-chip microsupercapacitors[1,2]. To avoid battery-like behavior it is crucial to select electrode material that doesn't interact with Lithium while providing efficient capacitive behavior and high electrical conductivity. To that purpose, using thermal ALD, noble metals are very good candidates but suffer from low nucleation[3]. This study aims to evaluate the implementation of ultrathin noble metals (such as platinum) deposited by ALD as electrodes for lithium-based capacitances.

Pt thin film was obtained by thermal ALD using Trimethyl(methylcyclopentadienyl)platinum(IV)and O_2 reactants. Pt nucleation on LiPON layers (20 nm thin) has been studied in comparison to lithium free substrates. In order to promote Pt nucleation surface treatment like TriMethylAluminium (TMA) pre-pulsing or TiN interfacial layer were used. Pt growth was morphologically, structurally and electrically characterized on SiO_2 and LiPON substrates using AFM, SEM, TOF-SIMS and spectroscopic ellipsometry.

Primarily, more than 300 cycles were required to obtain viable and continuous Pt film of 8nm on LiPON without any surface treatment. It was found that, whether using TMA pre-pulsing or a TiN interfacial layer, the nucleation delay could be reduced to 200 cycles on LiPON and 85 on SiO_2 substrate to achieve continuous Pt of 8 with a uniformity <3% and low resistivity (20 μΩ.cm) at 200mm wafer scale. Top view imaging and AFM characterizations show island growth without surface treatment on SiO_2 and LiPON substrates with high roughness. Same characterizations when TMA or TiN surface treatment is used evidence a high surface coverage with very low surface roughness on both substrates.

Focusing on the interface LiPON/Pt using TMA pre-pulsing, a thickness evaluation of LiPON with and without Pt capping under air exposure was performed using spectroscopic ellipsometry. Surprisingly, same behavior was observed in both cases. Ongoing interfacial characterizations are expected to assess the compatibility of these materials and Li diffusion through Pt.

(1) Göhlert, T. *Nano Energy* **2017**, *33*, 387–392.

(2) Ghandari, I. *Dalton Trans.* **2026**, *55* (3), 1149–1163.

(3) Hämäläinen, J. *Chem. Mater.* **2014**, *26* (1), 786–801.

8:15am **EM1-WeM-2 The Stability Study of ITO Film Deposited by Thermal Atomic Layer Deposition***, **Yongqing Shen**, Zhengying Jiao, Liguo Chai, Fengbin Tian, Kaiqiang Zhao, libin Jia, Jie Shen, Jianqi Chen, Jinjuan Xiang,* Beijing Superstring Academy of Memory Technology, China*; Weihan Fan,* Beijing Superstring Academy of Memory Technology, Taiwan*; Hongbo Sun, Guilei Wang, Chao Zhao,* Beijing Superstring Academy of Memory Technology, China

Metal oxide thin-film transistors (TFTs), especially InGaZnO TFTs have attracted considerable attention for 3D dynamic random access memory (DRAM) applications, owing to their lower off-state leakage and suitable carrier mobility. A thin Tin-doped In_2O_3 (ITO) has been employed as an inserting layer at contact region to reduce the Schottky barrier from IGZO channel, so as to get higher on-current. [1] Given the promising potential of ALD-grown ITO thin film for 3D DRAM applications, investigating its thermal stability and the impact of contact materials on its performance are critical for back-end-of-line (BEOL) compatibility evaluation.In this work, the thermal stability of ALD-grown ITO film was systematically evaluated via annealing experiments. The film is stable after annealing in an N_2 atmosphere at 600 °C, and has a mixed polycrystalline–amorphous phase structure. Prolonged annealing time, however, induced a significant increase in oxygen-related defects. When the annealing temperature was elevated to 800 °C, the ITO films became rough and initiated decomposition. Considering that ITO may come into contact with interconnect materials (e.g., TiN and W) during subsequent process integration, the effect of TiN deposition on ITO property was also investigated. Deposition of TiN at 530 °C in a hydrogen-containing ambient caused partial damage to the ITO film. In contrast, no obvious changes in ITO properties were observed after annealing in N_2 at 600 °C, indicating that reducing gases (e.g., H_2) can degrade ITO stability. At 400 °C (without H_2), TiN deposition did not cause significant ITO damage; nevertheless, a slight reduction in ITO thickness was detected. This thickness loss is speculated to result from reactions between the byproduct HCl and the ITO surface, as well as the breaking of In–O and Sn–O bonds due to oxygen scavenging by TiN. Collectively, the results demonstrate that the temperature, atmosphere, and process byproducts of subsequent steps all contribute to ITO film damage or thickness loss. This study provides reliable experimental data to guide the integration of ITO for advanced 3D DRAM applications.

8:30am **EM1-WeM-3 Atomic Layer Deposition of TiN layer in Interposer Chip for Superconducting Quantum Processor Unit***, **Kestutis Grigoras**, Harshad Mishra, Jukka-Pekka Kaikkonen, Joel Hätinen, Elsa Mannila, Wisa Förbom, Rishabh Upadhyay, Mikael Kervinen, Isabel Gueissaz-Mattelmäki, Marco Marin Suarez, Jorden Senior,* VTT Technical Research Centre of Finland, Ltd, Finland

The increasing complexity of interconnects on a chip and the potential for crosstalk between qubits present significant challenges for scaling up a superconducting quantum processor unit (QPU). The commonly adopted solution is 3D integration, where a QPU interposer chip is employed to reduce parasitic capacitance and inductance, as well as to facilitate signal routing between qubits and control electronics. For higher levels of integration, the interposer typically incorporates through-silicon vias (TSVs). The purpose of TSVs is to minimize the so-called chip resonance mode and to route signals between qubits and control electronics. Due to the growing density of interconnects, the diameter of superconducting TSVs must be as small as possible, on the order of several tens of micrometers. The most reliable method for conformally coating the sidewalls of such high-aspect-ratio structures is the atomic layer deposition (ALD) technique. There are only a few material candidates suitable for superconducting coatings, with titanium nitride (TiN) being one of them.

In this work, we have fabricated and tested silicon interposer chips with coplanar waveguide (CPW) type signal lines and resonators formed by patterned TiN/Ta or Nb layers. These structures were prepared by sputtering [1]. Several types of TSVs were etched using deep reactive ion etching (DRIE) and then coated with a TiN layer using either thermal or plasma ALD. The performance of these structures was measured and compared to reference chips without TSVs. We also compared different characteristics of TiN layers obtained by sputtering and by thermal or plasma ALD. We found that both the microstructure and the critical temperature (T_c) of TiN films prepared by different methods were quite similar. On the other hand, the film stress and selectivity in wet or dry etchants depended on the preparation method, with differences reaching even an order of magnitude. Depending on the fabrication step, these differences could either complicate or, conversely, simplify chip fabrication.

K. Grigoras et al., “Qubit-compatible substrates with superconducting through-silicon vias”, IEEE Trans Quant Eng, 3 2022, doi:10.1109/TQE.2022.3209881
[https://doi.org/10.1109/TQE.2022.3209881]

8:45am **EM1-WeM-4 Achieving Ultra-Low Resistivity in TiN Thin Films via Supercycle PEALD: The Critical Role of Ti:N Stoichiometry over Impurity Content***, **Van Long Nguyen**, Christophe Vallee, Natalya Tokranova, Bryant Colwill,* University at Albany-SUNY

Titanium nitride (TiN) has attracted significant interest in microelectronics due to its excellent chemical resistance, thermal stability, and low resistivity. Low-resistivity, stoichiometric TiN films are essential for realizing high-performance interconnects, diffusion barriers, and electrodes in next-generation microelectronic and quantum devices. While Atomic Layer Deposition (ALD) offers superior conformality, conventional low-temperature processes often yield nitrogen- or titanium-deficient films with high electrical resistivity due to poor stoichiometry and excessive impurity incorporation. We introduce a supercycle PEALD approach that periodically alternates two distinct plasma chemistries (TMSDMA + Ar plasma and TMSDMA + N_2/H_2/Ar plasma with bias to play with energetic ions) (**Figure 1Sa and 1Sb**) to precisely control the TiN film composition and structure. The resulting TiN supercycle film demonstrates a significantly lower electrical resistivity than its constituent films (**Figure 1Sc**). Surprisingly, this performance gain is achieved even with relatively high residual concentrations of C and O impurities. XPS analysis confirms that the resistivity minimum directly correlates with an approximately stoichiometric Ti:N ≈ 1:1 ratio derived from the relative populations of TiN-related Ti2p and N1s chemical states (**Figure 1Sc**). This result indicates that precise Ti:N stoichiometry, rather than impurity concentration, is the dominant factor governing the electrical performance of TiN films. This supercycle strategy provides a scalable, low-temperature method for fabricating high-conductivity TiN suitable for advanced nanodevice integration.

9:00am **EM1-WeM-5 Characterization of Superconducting Niobium Nitride Thin Films Grown by Thermal Atomic Layer Deposition***, **Annika Häkkinen**, Oona Turpeinen, Jaakko Julin,* University of Jyväskylä, Finland*; Mikko Laitinen,* University Of Jyväskylä, Finland*; Timo Sajavaara,* University of Jyväskylä, Finland

Metal nitrides are a promising group of superconducting materials for a wide range of quantum technologies and advanced electronic applications. In applications requiring superconducting functionality, such as quantum computing, thin-film quality plays an essential role in device performance. Among metal nitrides, niobium nitride (NbN) is especially interesting due to its relatively high theoretical critical temperature (17 K) and compatibility with thermal ALD processes, which provide a straightforward implementation without added process complexity. [1]

In this work, superconducting NbN thin films were grown with TFS-200 ALD system from Beneq Oy operated in thermal mode at 400–500 °C using $NbCl_5$ and NH_3 as precursors. Film thicknesses varied between 25 and 100 nm and the depositions were done on silicon and sapphire substrates. The effects of film thickness, deposition temperature, substrate choice, and post-deposition annealing (650–1000 °C) on the superconducting and structural properties were investigated. Film characterization was carried out using electrical resistivity and critical temperature measurements,

Atomic Force Microscopy (AFM), X-Ray Diffraction (XRD), and Time-of-Flight Elastic Recoil Detection (ToF-ERD).

Deposited films exhibited promising superconducting properties with critical temperatures up to 13.6 K after post deposition annealing. Films were slightly nitrogen rich and contained low concentrations of impurities such as O (< 4.6 at.%), Cl (< 3.6 at.%), C (< 3.8 at.%) and H (< 4.7 at.%). Superconducting critical temperature was dependent on the film thickness but even the thinnest films (25 nm) had a transition temperature of 10.6 K. These results highlight thermal ALD as a viable method for producing high-quality superconducting NbN thin films.

[1] G. K. Deyu et al." Recent advances in atomic layer deposition of superconducting thin films: a review" *Mater. Horiz*. **12**(15):5594-5626 (2025)

Emerging Materials and Processes
Room Tampa Bay Salons 1-2 - Session EM2-WeM

Energy-enhanced ALD

Moderators: John Conley, Oregon State University, **Jean-François de Marneffe**, IMEC

10:45am **EM2-WeM-12 Let There Be Light: Photo-Assisted ALD of Pt Using $Pt(acac)_2$ and O_3***, **Robin Petit**, Kinanti Aliyah, Matthias Minjauw, Ruben Blomme, Arno Depoorter, Seppe Van Dyck,* Ghent University, Belgium*; Martin Rosenthal,* ESRF, France*; Zeger Hens, Christophe Detavernier, Jolien Dendooven,* Ghent University, Belgium

Global trends such as the transition to green hydrogen production and advancements in microelectronics are increasing the demand for high performance Pt-based electrodes. ALD enables Pt deposition in various morphologies, from size-controlled nanoparticles to continuous thin films, by tuning the nucleation behaviour and the number of ALD cycles. In thermal and plasma-enhanced Pt ALD, nucleation depends on parameters such as temperature, precursor dose, co-reactant choice, and substrate pretreatments.

This work focuses on photo-assisted ALD (photo-ALD), which uses ultraviolet (UV) illumination as an additional parameter to control growth. Building on our earlier study using $MeCpPtMe_3$ and O_2, where photon-precursor interactions enabled lower temperature Pt growth with shorter nucleation delays [AVS-ALD2024], we developed a new Pt photo-ALD process using $Pt(acac)_2$ and O_3 under 365 nm illumination. $Pt(acac)_2$ is a more economically viable precursor due to its straightforward synthesis and established large-scale production.

Continuous illumination at 100°C results in metallic Pt (Fig. 1a) and increased Pt loading compared to thermal ALD. To investigate nucleation and growth, in-situ X-ray fluorescence (XRF) and grazing-incidence small angle X-ray scattering (GISAXS) were performed at the European Synchrotron Radiation Facility (ESRF). Tracking the Pt growth kinetics with XRF reveals an enhanced nucleation with illumination (Fig. 1b). GISAXS indicates that, at similar Pt loading, photo-ALD produces smaller particles with higher areal density, while thermal ALD yields larger particles with wider spacing (Fig. 2). SEM images confirm these trends and show a broader size distribution for thermal ALD, indicating more disordered growth where nucleation and particle growth occur simultaneously (Fig. 3).

To understand the impact of photon-precursor interactions during each ALD step, the timing of the illumination is varied, showing that illumination during the $Pt(acac)_2$ half-cycle is critical to achieve photo-enhancement, yet reaction with O_3 remains necessary for further ALD growth. Notably, enhanced growth occurs not only when illuminating the precursor in the gas phase: illuminating surfaces bearing adsorbed $Pt(acac)_2$ and then dosing additional precursor, before the O_3 step, also increases Pt uptake relative to thermal ALD. Ongoing spectroscopy studies aim to clarify the effect of illumination on the precursor ligands.

In summary, our work shows that UV-illumination promotes Pt nucleation for both $MeCpPtMe_3$- and $Pt(acac)_2$-based ALD, providing insights that support the development of photo-ALD for other metals and advance the technique toward practical applications.

11:00am **EM2-WeM-13 Microwave Enhanced Atomic Layer Deposition (MW-ALD) of Ta2O5***, **Jessica Haglund**,* Oregon State University*; John Conley, Jr.,* Oregon State Univesity

A limitation of some ALD processes is the required low deposition temperature. Low temperature can allow incorporation of residual impurities from unreacted precursors which in turn may degrade electrical, physical, and optical properties. A way to reduce impurities and improve film quality while still maintaining a low thermal budget is known as energy enhanced ALD (EE-ALD), in which extra energy is incorporated into the ALD cycle to improve the film while it is growing. EE-ALD using *in-situ* treatments with either rapid thermal, flash lamp, plasma, or UV exposure have all demonstrated improvements over standard ALD films.[2-10] We recently demonstrated a new EE-ALD technique we call microwave enhanced ALD (MW-ALD) using Al_2O_3.[11] Here we present MW-ALD results on Ta_2O_5 and compare with MW-ALD of HfO_2 and Al_2O_3.

MW-ALD of Ta_2O_5 was performed at 120 and 200 °C using $Ta(OEt)_5$ and H_2O using a Picosun R200 modified with a custom MKS microwave generator and helical antenna. 400 W MW exposures (without plasma generation) were performed following the $Ta(OEt)_5$ purge, starting 15 s into the 120 s N_2 purge and lasting for 30 s. Film thickness and refractive index were analyzed using a mapping Film Sense FS-1 ellipsometer.

On Pt substrates, MW exposure at both 120 and 200 °C resulted in improved uniformity, an increase in median Ta_2O_5 thickness from 8.1 to 8.7 nm, and a slight increase in refractive index. For Si substrates, MW exposure at 200 °C also improved uniformity but had the opposite impact, reducing Ta_2O_5 median thickness from 5.7 to 4.7 nm. For HfO_2 (TEMA-Hf/H_2O), MW pulses during the TEMA-Hf purge resulted in a ~50% increase in thickness and an increase in refractive index, while MW during the H_2O purge had minimal impact. For Al_2O_3 (TMA/H_2O), MW exposure during the TMA pulse improved film quality compared to exposure during the H_2O pulse.Additional investigation of MW exposure during other parts of the ALD cycle, thicker depositions, and electrical data on MOS and MIM devices will be presented at meeting.

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11:15am **EM2-WeM-14 Electron-Enhanced Atomic Layer Deposition of Tunable TiCxNy Ternary Nitride Films Using Tetrakis(dimethylamido)titanium with Ammonia Reactive Background Gas***, **Zachary Sobell**, Andrew Cavanagh, Steven George,* University of Colorado at Boulder

Electron-enhanced atomic layer deposition (EE-ALD) of amorphous tunable titanium carbonitride (TiC_xN_y) films was obtained at low temperatures. Amorphous ternary nitrides are important as diffusion barriers for back-end-of-the-line metallization in microprocessor fabrication. The TiC_xN_y EE-ALD was achieved using sequential exposures of tetrakis(dimethylamido)titanium (TDMAT) and low energy electrons in the presence of a continuous NH_3 reactive background gas (RBG) (**Figure 1**). The composition of the TiC_xN_y films was tuned by varying the NH_3 background pressure and the electron exposure time. The TiC_xN_y EE-ALD was performed utilizing a hollow cathode plasma electron source (HC-PES). The HC-PES delivered a high electron flux into background gases at pressures up to several mTorr. TDMAT was used as the source of Ti, C, and N. The NH_3 RBG served both as a source of additional N and a method for the removal of C from the TiC_xN_y films. The TiC_xN_y EE-ALD film growth was monitored using in situ ellipsometry. The TiC_xN_y EE-ALD was conducted at temperatures of 30-130°C using NH_3 pressures of 0 to 3 mTorr.

The C content in the TiC_xN_y films could be tuned using the NH_3 RBG pressure (**Figure 2**). Lower NH_3 pressures led to the incorporation of more C into the TiC_xN_y films. The C:Ti ratio varied from ~0.3 to ~0.05 as measured by XPS at a constant electron exposure time of 10 s. Electron exposure time was also used to modulate the C content in the TiC_xN_y films (**Figure 3**). Shorter electron exposures led to more C incorporation. The C:Ti ratio varied from ~2 to ~0.1 as measured by XPS at a constant NH_3 background pressure of 2 mTorr. In situ 4-wavelength and ex situ spectroscopic ellipsometry were able to estimate electrical resistivities for the TiC_xN_y films. Resistivity decreased from >2000 μΩ-cm to ~200 μΩ-cm with decreasing C content. XRR measurements were able to determine film densities. The film density for TiN films was 4.6 g/cm^3 and the film density decreased with increasing C content.

The C content in the TiC_xN_y films could also be varied using a CH_4 RBG. Carbon could be added by carbon EE-CVD using electron exposures together with CH_4 RBG. The carbon could also be removed using electron exposures together with NH_3 RBG. However, the C content in TiC_xN_y films was difficult to control using a supercycle approach with TiN EE-ALD and carbon EE-CVD.

11:30am **EM2-WeM-15 Pulsed Excimer Laser Processing to Promote Room-Temperature Crystallization of ALD HfO_2 Films**, ***T. Jude Kessler***, *Hans Cho, John P. Murphy, Sarah Brittman, Saikat Mukhopadhyay,* 1. US Naval Research Laboratory*; Peter Litwin,* 2. NRC Research Associateship Program*; Bradley De Gregorio, Virginia Wheeler, F.K. Perkins, Margo Staruch,* 1. US Naval Research Laboratory

Ferroelectric hafnia compounds, including Hafnium Oxide (HfO_2), are of interest to realize advanced neuromorphic devices. The metastable, polar orthorhombic phase of HfO_2 is required to achieve the necessary ferroelectric device properties. Typically, this phase is stabilized at elevated temperatures, a significant barrier to producing thin films by atomic layer deposition (ALD). The lower deposition temperature of ALD enables direct, conformal integration of HfO_2 films on a variety of materials at any fabrication step but produces non-ferroelectric amorphous or monoclinic phase. Excimer Laser Annealing (ELA) has an edge over conventional annealing because it uses short laser pulses to heat only a thin surface layer, which rapidly cools due to a sharp thermal gradient with the underlying material. This process creates a heating and cooling cycle with insufficient time for the elevated state of the thin film to relax, promoting crystallization and stabilization of metastable phases. Thus, in this work, we apply ELA process to crystallize ALD HfO_2 films and determine the parameters that produce the ferroelectric, orthorhombic phase.

Ultrathin (10-20 nm), amorphous HfO_2 films were deposited by plasma enhanced atomic layer deposition on thermal SiO_2 substrates at 200°C using TEMAHf and Ar/O_2 plasma. To enhance the absorption of the pulsed laser, all films were capped with 50nm PEALD TiN. Films were processed using 20ns ELA pulses from 308nm broad bandwidth XeCl Coherent COMPex 201 laser homogenized by a fly's eye system illuminating a 5mmx5mm square with gaussian temporal profile onto the film surface. Parametric ELA testing was initially conducted, varying fluence and number of pulses, to determine the experimental range with sufficient energy to alter the film without causing delamination or photochemical ablation. Experiments investigating the influence of raster pattern and fluence on resulting HfO_2 structure were then performed.

Initial results show that controlling the ELA process parameters, we can both crystallize and influence the phase of HfO_2 films produced. Crystalline films were achieved without any observed damage to the film or underlying surface, exemplifying an advantage of ELA. Using TEM and glancing-incidence x-ray diffraction (GIXRD), we identified the ability to stabilize films with either orthorhombic, tetragonal, or a combination of both phases. Under the right parameters, films were single phase without any residual amorphous or monoclinic phase. Details establishing process-structure-property relationships using this promising technique to achieve relevant and scalable ferroelectric films will also be discussed.

11:45am **EM2-WeM-16 Thermally Activated Atomic Layer Annealing (ALA): A Plasma Free Approach to Densification of Hafnia Thin Films**, ***Dushyant Narayan***, *Thi Thu Huong Chu, Dan Le, Minjong Lee, Doo San Kim, Soham Shirodkar, Jean-Francois Veyan, Jiyoung Kim,* The University of Texas at Dallas

As device length scales continue to scale and transition from 2D planar to 3D structures, device architectures require precise control of step coverage and involve increasingly stringent requirements on electronic performance of high-k dielectrics. One of the immediate challenges is achieving growth of high-k dielectric materials with low defectivity and high density in high-aspect-ratio (HAR) structures within a low thermal budget. In this regard, Atomic layer annealing (ALA) methods offer low-temperature deposition with superior film quality compared to conventional thermal ALD, which has been reported for nitride-based materials such as AlN, and GaN.[1-3]These ALA methods typically utilize plasma to transfer energy to the film during growth to facilitate the migration of adatoms on the surface and also eliminate unreacted ligands, leading to a more organized and compact thin film.[4] However, plasma based methods suffer from serious limitations in high-aspect ratio structures, where plasma recombination effects can limit the concentration of plasma radicals in trenches.

In this work, we will discuss a chemical approach to densification which we term Thermal-ALA. This method is plasma-free, enabling deposition in HAR structures, and introduces a chemical annealing step into the reaction chamber after each deposition cycle. Here, we will present *in-situ* characterization of the reaction mechanisms involved in this process via Reflective Absorption Infrared Spectroscopy (RAIRS) as well as *ex-situ* characterization of the resulting film properties. By varying the dose of oxidant and substrate temperature we show that resulting hafnia films grown with this technique have improved wet-etch rate (WER), density, and can even crystallize during deposition at substrate temperatures as low as 300 °C. By demonstrating this technique, we show that densification of hafnia thin films can be achieved with purely thermal and chemical techniques, thereby providing another engineering parameter by which film properties can be controlled.

This work is supported by Samsung Electronics through the GRO program(IO250621-13116-01).

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ALD Applications

Room Ybor Salons I-IV - Session AA-WeA

Novel ALD Applications

Moderators: Jessica Jones, Argonne National Laboratory, **Austin Minnich**, Caltech

1:30pm **AA-WeA-1 Nanolaminate Bragg Reflectors for Acoustic Phonons in the > 100 Ghz Range*, John Murphy**, Jeremy Robinson, Maxim Zalalutdinov, Kyle Munson, Jeffrey Woodward,* U.S. Naval Research Laboratory

Nanolaminates grown by atomic layer deposition (ALD) offer a well–controlled platform capable of confining longitudinal acoustic (LA) phonons in > 100 GHz regime through engineered Bragg reflection. LA phonons in this frequency range strongly influence thermal and electronic behavior and require individual layers of Bragg reflectors to be < 10 nm thick with sub-nm roughness, while providing high contrast in acoustic impedance. ALD is unique in its ability to produce nanolaminate Bragg reflectors through sequential growth of ultra-thin, uniform, and low–roughness amorphous multilayers; with tailorable acoustic impedances through material selection. An ALD-based approach also allows conformal coating on planar and three–dimensional geometries where current state-of-the-art GaAs/AlAs, or other epitaxially grown superlattices cannot be realized. Additionally, the semi-surface-agnostic nature of the amorphous oxide ALD growth provides a route for integrating phononic mirrors, cavities, and filters into a variety of a fabrication flows in addition to well-established devices platforms, opening opportunities for next–generation acousto–optic and acousto–electronic systems compatible with current and emerging MEMS architectures.

In this work, we report results for Al_2O_3/HfO_2 nanolaminates grown via ALD using layer design guided by transfer–matrix simulations and targeting LA phonons in the frequency range 100-500 GHz. Effective sound speeds and mass densities of both single–layer films and stacked nanolaminates are extracted via ultrafast pump-probe measurements and x–ray reflectivity, respectively, allowing elastic properties to be correlated with ALD growth conditions. We compare the simulated spectral response for phonon lifetime with pump–probe measurements using ultrathin optoacoustic transducer layers that act both as acoustic cavities and a source of optically generated strain pulses. Exploiting this architecture, we are able to validate simulated reflection response with thin optoacoustic transducer layers deposited directly onto nanolaminate films. These results establish ALD nanolaminates as a tunable, integrable platform for GHz–sub–THz phonon control and phononic component design beyond conventional epitaxial III–V and nitride superlattice systems.

1:45pm **AA-WeA-2 Next Generation ALD Functionalization of Lead-free MCPs for the Photomultiplier Tube: HRPPD*, Stefan Cwik**, Melvin, J. Aviles, Stephen M. Clarke, Matthew Grden, Cole J. Hamel, Alexey V. Lyashenko, Mark A. Popecki,* Incom Inc.*; Jeffrey W. Elam,* Argonne National Laboratory, USA*; Michael J. Minot,* Incom Inc.

Microchannel plates (MCPs) find application in image intensifier tubes for night vision goggles, in spectrometers, and in photo multiplier tubes (PMTs) for time-of-flight (TOF) measurements based on their high resolution, ultra-fast timing (10-50 ps) and high gain (>10^4). Conventionallead glass MCPs have been the industry standard since the 1960s. The manufacture includes a hydrogen firing step in which lead oxide gets reduced to bring the plate to target resistance and to simultaneously generate the electron emission layer limiting the adjustability of the MCP properties to target applications.

Incom Inc. has commercialized the ALD-GCA-MCP technology, applying ALD technology from Argonne (ANL) on Incom's glass capillary array (GCA) substrates. The physically and chemically robust silicate glass allows the fabrication of large area GCAs up to 20x20 cm^2 and the high substrate resistance enables functionalization by ALD. ALD functionalization of the GCA comprises resistive and emissive layers. The resistive layer is a tunable nanocomposite of conductive and insulating materials and defines most electrical characteristics of the MCP since it serves as a strip layer to recharge the emissive layer during operation. The emissive layer is composed of a high secondary electron yield material like MgO or Al_2O_3 to maximize gain for intensifier applications.

Incom's 1st generation MCPs rely on the combination of Incom proprietary Chem1 resistive coating and MgO emissive coating, which provide high gain stability and durability for open MCP applications in space-flight applications. However, for application in sealed MCP-PMTs, high gain in dry UHV and minimum out-gassing are critical to limit the effects of after-pulsing. This maximizes the device lifetime, crucial for long-term applications such as TOF experimentation in Electron Ion Collider programs. Herein, we report the performance of Incom's new proprietary halide-free Chem5-MgO MCP technology in sealed MCP-PMTs such as Incom's 10x10 cm HRPPD, which was developed to optimize the application specific MCP characteristics. The Chem5-MgO performance under dry UHV conditions is compared with MCPs based on Chem1-MgO chemistry used in HRPPDs. Notably, the higher gain provided by Chem5 allows lower voltage operation (ΔV=200V) thereby reducing electric fields in the PMT and minimizing after-pulsing. Large area MCPs with the advanced Chem5-MgO coatings are also being incorporated into Incom's LAPPD, the world's largest planar MCP-PMT.

This work was supported by the US Department of Energy (NNSA), DE-SC0018778

2:00pm **AA-WeA-3 Growing Grass for the Stars: Conformal Nanostructured Ar Coatings for Astronomical Micro-Optics*, Ishan Rana**, Suvrath Mahadevan,* Pennsylvania State University

Many Astronomical Instruments require high precision micro-optics with complex free form geometries. A new and attractive choice to fabricate such microoptics is the IPX clear photoresin, this resin offers very high internal transmission (>99.9%) in the visible and near infra-red wavelength range and has excellent shape fidelity. However, fresnel reflections at the air-polymer interface introduce significant photon loss (~4%). This is detrimental for photon starved fields like astronomy. To reduce photon loss we need to apply antireflective coatings on the microlenses. However, due to the complex shape of the microlenses we need highly conformal coatings. We use Atomic Layer Deposition to create these AR coatings.

In our project, we study the application of grass-like anti reflective coatings on IPX clear micro-optics. These coatings are created by first depositing alumina using thermal ALD on the microlenses and then generating nanostructures on the surface of the alumina by treating the samples in de-ionized water. The treated samples with nanostructured surfaces can then again be coated with various other materials like SiO_2, TiO_2, and HfO_2 to create a multilayer grass like coating. These coatings mimic a gradient change in refractive index, suppressing surface reflections. Such coatings can improve average transmission from 91.9% up to 99%

While in previous work ALD has been used to coat micro-optics, we demonstrate here for the first time application of ALD on micro-optics with nanostructured surfaces and the antireflective performance of such coatings, as well as discuss the challenges and process steps of such applications.

2:15pm **AA-WeA-4 Electrochemical Oxidation of Perfluorobutanoic Acid using ALD Thin Film Electrocatalysts Deposited on Reactive Electrochemical Membranes*, Saurabh N Misal**, Argonne National Laboratory, USA*; Atefeh Nadeali, Brian P Chaplin,* University of Illinois at Chicago*; Jeffrey W Elam,* Argonne National Laboratory, USA

Electrochemical oxidation of per- and polyfluoroalkyl substances (PFAS) using Magnéli-phase titanium suboxide (Ti_nO_{2n-1}) reactive electrochemical membranes (REMs) is a promising and effective approach for mineralizing concentrated PFAS wastes. Still, it can lead to the accumulation of short-chain PFAS as byproducts. Perfluorobutanoic acid (PFBA) is one such short-chain product observed during PFAS oxidation and is also commonly detected in groundwater and industrial wastewater. Due to its low hydrophobicity, low polarizability, and high mobility, PFBA adsorbs poorly at the anode surface, leading to sluggish kinetics. In this work, we focused on the synthesis of an electrocatalyst using atomic layer deposition (ALD) on REMs to further enhance the removal and defluorination of PFBA during oxidation. In the first part of the study, thin films of SnO_2, Sb_2O_5, and Pd were deposited on REMs. For the ALD process, the reactor temperature, precursor dose time, and number of cycles were optimized for high-aspect-ratio (~5000) REMs. The synthesized electrocatalytic REMs were characterized using X-ray photoelectron spectroscopy to confirm oxidation states of the electrocatalyst. Moreover, top surface and cross-sections of the REMs were mapped using scanning electron microscopy with energy-dispersive X-ray spectroscopy. In the second part of the study, the synthesized REMs were tested for the electrochemical oxidation of ~21 mg L^{-1} PFBA in a flow-through reactor at a constant potential and flux. The permeate samples collected from oxidation experiments were analyzed using ion chromatography. At 150 L m^{-2} h^{-1} permeate flux and a constant potential of 3.6 V/SHE, ~80% PFBA was removed with ~100% fluorine recovery using thin-film-deposited REM. The analysis showed the presence of trifluoroacetic acid and perfluoropropanoic acid in μg L^{-1} levels (10—20% product yield), along with the formation of fluoride ions in mg L^{-1} levels (80—90% fluoride yield). In the final part of the study, insulating TiO_2 films were deposited on the synthesized electrocatalytic REM by ALD to suppress

oxygen evolution side reaction, and electrochemical oxidation of PFBA was tested using the synthesized thin-film-deposited REM.

2:30pm **AA-WeA-5 Development of an Atomic Layer Deposition System for Tritium Permeation Barriers on Arbitrary Geometries**, ***Zachary Robinson,*** University of Rochester*; Jeffrey Woodward,* NRL*; Alexander Kozen,* University of Vermont*; Tyler Liao,* University of Rochester*; Soren Bentley,* UKAEA, UK*; Luke Herter, Rashad Ahmadov, Josh Ruby, Mark Wittman, Matthew Sharpe,* University of Rochester

Atomic layer deposition (ALD) is an ideal technique for deposition of films on arbitrarily shaped containers such as those used to contain tritium for fusion applications. In this work we present the design, construction, and initial experimental results from a custom ALD system built to deposit hydrogen isotope permeation barriers. This challenge is motivated by the extreme difficulty of producing and containing tritium while mitigating losses. The ALD films developed in this project could be used to filter, purify, store, and transport tritium, increasing the efficiency of Fusion fuel management.

The primary benefit of our ALD system is the ability to deposit films on arbitrarily shaped surfaces, such as the interior walls of tubing and canisters used to contain tritium. In our initial experiments, we deposited thermal ALD alumina films on both silicon wafers and planar copper foil substrates. Characterization with ellipsometry yielded ALD growth rates of~1.1 Å/cycle for temperatures between 100 °C and 210 °C on the Si witness samples. X-ray photoelectron spectroscopy (XPS) on both the Cu foils and Si substrates indicates stoichiometric Al_2O_3. To quantify the permeation reduction factor (PRF) of the of the ALD films, the permeability of deuterium through 25 µm Cu-foils coated with 10 nm of alumina was measured. It was found that thin ALD films have a PRF of around 25 at permeation temperatures between 275 °C and 350 °C.

Following our initial characterization of the system, a 1 L type 316 stainless steel (SS316) canister was installed in our ALD reactor, with 10 silicon witness samples mounted throughout the interior volume of the canister. ALD process conditions were systematically varied, and the uniformity of the alumina films throughout the volume of the canister was optimized such that the inlet side of the reactor was about 10% thicker than the outlet. All of the witness samples had sub-nm roughness. Experiments were also performed on highly polished SS316 to compare film properties between the Si and the stainless substrates. XPS indicates that an aluminum hydroxide forms on SS316 for growth temperatures below 200 °C. Experiments are currently underway to fill a canister with tritium and study the residual gases that exist in the canister as a function of time.

2:45pm **AA-WeA-6 Argon Ion Implantation in ALD PbTe Thin Films for Phonon Engineering**, ***Haifeng Cong,*** *Helmut Baumgart,* Old Dominion University

Lead telluride (PbTe) is a promising thermoelectric material due to its high Seebeck coefficient and large figure of merit (ZT) at elevated temperatures. While atomic layer deposition (ALD) enables high-quality PbTe thin films, strategies to enhance thermoelectric performance via phonon engineering remain limited.In this study, PbTe thin films were grown on silicon substrates with native oxide using thermal ALD, employing $Pb(C_{11}H_{19}O_2)_2$ and $(Me_3Si)_2Te$ as precursors. Films were deposited at 130–170 °C under 500 mTorr, following surface functionalization to ensure reproducible chemisorption. To engineer phonon transport, argon ions were implanted at 180 keV with a fluence of 1×10^{15} cm^{-2} and subsequently annealed to generate controlled lattice defect clusters.The effects of implantation were characterized using X-ray diffraction (XRD) for crystal structure, FE-SEM and AFM for morphology and roughness, TEM to directly observe defect profiles, and EDS for composition and stoichiometry. Seebeck coefficient, Hall effect, and thermal conductivity measurements were conducted to assess the impact of defects on thermoelectric performance.Results demonstrate that argon implantation introduces well-distributed lattice defects, effectively scattering phonons and reducing thermal conductivity without significant degradation of electrical properties, leading to enhanced ZT. These findings highlight defect engineering via inert ion implantation as an effective route to improve the thermoelectric performance of ALD PbTe thin films.

3:00pm **AA-WeA-7 Multifunctional Hierarchically Restructured Antibacterial Neural Interfacing Electrodes via Plasma-Enhanced Atomic Layer Deposition**, ***Shahram Amini,*** Drexel University*; Feng Gang, Henna Khosla,* Villanova University*; Wesley Seche, Kriti Panchal, Steve May, Ekaterina Pomerantseva,* Drexel University*; Jacob Elmer,* Villanova University*; Gregory Caputo, Jeffrey Hettinger,* Rowan University

Next-generation neural and cardiac implantable electrodes are increasingly constrained by the coupled requirements of miniaturization, electrochemical performance, and resistance to bacterial colonization. Hierarchical Surface Restructuring (HSR™) enables substantial amplification of electrochemically active surface area on metallic electrodes, thereby addressing charge-transfer limitations associated with geometric scaling. However, translating these surface architectures into long-term implantable devices requires additional surface-level functionality to mitigate infection risk without degrading electrochemical efficiency. In this work, plasma-enhanced atomic layer deposition (PEALD) is employed as a conformal, thickness-controlled surface-engineering strategy to functionalize HSR™ Pt–10Ir electrodes with ultrathin ZnO-based films. The self-limiting reaction chemistry of PEALD enables uniform coating of complex micro- and nanoscale features while preserving the underlying hierarchical morphology. By modulating plasma chemistry during deposition, ZnO films with distinct phase compositions are integrated onto HSR™ electrodes, enabling independent tuning of antibacterial and electrochemical responses. Antibacterial activity is demonstrated under dark, aerobic conditions, decoupling the observed bactericidal behavior from photocatalytic mechanisms and establishing controlled Zn^{2+} ion release as the dominant mode of action. Simultaneously, select ZnO–Zn nanocomposite coatings enhance electrochemical performance, exhibiting reduced impedance and increased charge storage capacity relative to uncoated HSR™ electrodes. Collectively, these results establish PEALD as a scalable and manufacturing-compatible approach for introducing multifunctionality onto hierarchically restructured neural interfacing electrodes, providing a practical pathway toward infection-resistant bioelectronic interfaces that maintain high electrochemical performance under clinically relevant conditions.

3:15pm **AA-WeA-8 ALD Al_2O_3 on Nanocellulose Substrates – Tailoring Barrier and Wetting Properties for Food Packaging**, ***Hugo Patureau,*** SIMAP, Grenoble-INP, CNRS, France*; Chloé Parisi, Julien Bras,* LGP2, France*; Erwan Gicquel,* CILKOA, France*; Frédéric Mercier,* SIMAP, Grenoble-INP, CNRS, France*; Elisabeth Blanquet,* SIMAP, grenoble-INP, CNRS, France*; Arnaud Mantoux,* SIMAP, Grenoble-INP, CNRS, France

Cellulosic products are a promising alternative to plastics for food packaging due to being biodegradable and recyclable. Nanocellulose is especially promising in the food packaging industry due to high oxygen barrier performances. However, high moisture sensitivity leads to poor water vapor barriers while also compromising oxygen barrier performance under humid conditions. Recent studies have shown that Al_2O_3 deposited by atomic layer deposition (ALD) on cellulosic substrates increases water vapor and oxygen barrier performance and grants hydrophobic properties [1–4]. However, the influence of ALD process parameters on the performances obtained remain insufficiently explored.

In this work, we demonstrate how deposition temperature, number of ALD cycles and different co-reactants (H_2O, O_2 plasma and ethanol) govern the water vapor barrier and wettability performance of Al_2O_3 films on different nanocellulose substrates. Findings demonstrate a significant increase in wettability using few ALD cycles of TMA and ethanol as co-reactant (figure 1), with correlations observed between wettability and surface energy, surface chemistry, and film morphology. Water vapor transmission rates (WVTR) were measured and also displayed a high dependence on deposition temperature, ALD cycles and co-reactants (figure 2). Experiments revealed a critical thickness of Al_2O_3 on nanocellulose, where no reduction of WVTR was observed beyond that point. The results highlight the critical role of ALD processing conditions in developing high performance nanocellulose food packaging.

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ALD Fundamentals: Growth and Characterization
Room HB Plant Ballroom - Session AF1-WeA

Modeling for ALD Processes I

Moderators: Alex Martinson, Argonne National Laboratory, **Paul Williams**, Pegasus Chemicals

1:30pm **AF1-WeA-1 A Framework Bridging Generative AI Models and Atomic Layer Deposition for $HfxZr_{1-x}O_2$, *Han-Bo-Ram Lee***, *Bonwook Gu,* Incheon National University, Republic of Korea

As atomic layer deposition (ALD) is increasingly applied to complex, multicomponent materials, selecting appropriate compositions and phase windows in practice still relies heavily on trial-and-error. This becomes a serious limitation for functional oxides, where small changes in composition can strongly affect phase formation and electrical properties under thin-film growth conditions. In this work, we present an inverse-design framework for ALD, a general approach that connects recent advances in data-driven artificial intelligence (AI) models for inorganic materials with experimental ALD process development. We first generate many candidate crystal structures by using an AI-based structure generator (a model that proposes plausible crystal structures from composition). This generator prioritizes physically reasonable inorganic structures and compositions, as well as thermodynamically stable candidates (i.e., structures likely to form). These structures are relaxed with machine-learning interatomic potential (a fast surrogate for DFT) to obtain consistent formation energies and the energy above the convex hull (E_{hull}), enabling fast thermodynamic screening across composition. Based on this thermodynamic screening, graph neural network models are used to estimate key electronic properties, allowing composition–structure–property trends to be mapped without extensive first-principles calculations. The framework is demonstrated using the Hf–Zr–O dielectric system. The model captures a clear trade-off between band gaps and dielectric response across composition and highlights an intermediate composition range where low-energy tetragonal and orthorhombic phases are frequently predicted. Guided by these results, $Hf_{1-x}Zr_xO_2$ thin films were deposited by atomic layer modulation (ALM; an ALD sequencing method that tunes the Hf/Zr ratio cycle-by-cycle), which enables atomic-scale control of cation ratios within a single ALD sequence. Structural, electrical, and optical measurements show that the predicted phase evolution and property trends are reproduced experimentally, confirming that the model-guided design window remains meaningful under realistic ALD conditions. Overall, this framework provides a practical way to reduce empirical trial-and-error in ALD by focusing experiments on the most promising composition and phase regions. Although demonstrated here using a Hf–Zr–O system, the framework is not material-specific and can be readily applied to other complex oxides, doped systems, and emerging ALD materials.

1:45pm **AF1-WeA-2 Quantitative Kinetic Monte Carlo Modeling of Al_2O_3 Atomic Layer Deposition by Trimethylaluminum Based on Neural-Network-Potential-Derived Kinetics**, ***Yichen Zou***, *Yuxuan Wu, Jun Yamaguchi, Noboru Sato, Atsuhiro Tsukune, Yukihiro Shimogaki,* The University of Tokyo, Japan

Atomic layer deposition (ALD) is a key thin-film growth technique in advanced semiconductor manufacturing, enabling atomic-scale thickness control and excellent conformality. Despite the technological maturity of the trimethylaluminum (TMA)–H_2O process for Al_2O_3, establishing a quantitative link between atomistic surface reactions and experimentally observed growth behavior remains challenging due to the complexity of the reaction network, finite-temperature kinetic effects, and steric constraints on precursor adsorption.

In this work, we develop a kinetic Monte Carlo (KMC) framework for the TMA–H_2O ALD process by integrating molecular dynamics (MD) simulations with a neural network potential (NNP) trained to near density-functional-theory accuracy. Compared with our previous study, the present model introduces several key improvements. First, the sticking probability of TMA adsorption, previously approximated as an empirical constant, is re-evaluated using explicit MD collision simulations with a chemically irreversible adsorption criterion, yielding a lower and more realistic value. This update enables more accurate estimation of adsorption timescales and surface saturation behavior. Second, the surface reaction network is substantially expanded to explicitly include hydrogen migration as well as H_2O formation and desorption from hydroxyl groups, which were neglected in earlier modeling. Finally, steric effects arising from the bulky methyl ligands of intact TMA molecules are quantitatively incorporated into the KMC model through a local coordination-based descriptor that restricts adsorption in crowded environments.

The KMC simulations quantitatively reproduce key experimental growth characteristics of Al_2O_3 ALD. The simulated mass evolution within a single ALD cycle captures the characteristic rapid-then-slow mass uptake during the TMA pulse, followed by a negative mass change during the H_2O pulse associated with ligand removal and by-product desorption. The predicted saturated mass gain reaches 36.8 ng cm^{-2} $cycle^{-1}$ at 393 K, in good agreement with in situ quartz-crystal microbalance measurements. Furthermore, the simulations indicate that higher temperature and longer H_2O pulse duration promote more efficient removal of methyl ligands, leading to reduced residual carbon in the growing film. These trends highlight the importance of thermal activation and sufficient reactant exposure for minimizing carbon contamination during Al_2O_3 ALD. Overall, the combined treatment of MD-derived adsorption kinetics, expanded surface reaction pathways, and steric constraints provides a physically grounded and quantitatively improved description of Al_2O_3 ALD growth behavior.

2:00pm **AF1-WeA-3 Analysis and Design of Nb PE-ALD using Neural Network Potential Molecular Dynamics Simulation**, ***Noboru Sato***, *Akimasa Nakashima, Jun Yamaguchi, Naoki Tamaoki, Atsuhiro Tsukune, Yukihiro Shimogaki,* The University of Tokyo, Japan

Niobium (Nb) is a promising material for semiconductor interconnects, pMOS contacts, and superconducting components for Cryo-CMOS in quantum-computing applications. However, as a group-5 transition metal, Nb is difficult to reduce to the metallic state, and low-temperature CVD/ALD processes remain limited. We have been developing a low-temperature plasma-enhanced ALD (PE-ALD) process using $NbCl_5$ as a precursor and hydrogen plasma as a reducing agent. The resulting Nb films still exhibit high resistivity (~200 μΩ·cm), likely due to residual impurities and small grain size, compared with the bulk value (~15 μΩ·cm). In this study, we analyze the reaction mechanisms of $NbCl_5/H_2$ PE-ALD and explore process-design guidelines using molecular dynamics (MD) simulations based on neural network potentials (NNPs).Reaction analyses were conducted using NNP-based MD simulations implemented in MatlantisTM. The NNP was trained on PBE-based density-functional-theory data with empirical dispersion corrections. First, we examined saturated adsorption of $NbCl_5$ on the Nb(110) surface of body-centered cubic (bcc) Nb, a representative stable surface of metallic Nb. At low coverage, Nb and Cl atoms were largely dissociated on the surface; as coverage increased, Nb atoms aggregated, and at later stages chain-like $NbCl_4$ species formed on the surface.Next, we modeled plasma exposure by injecting H and Ar atoms onto the $NbCl_5$-saturated surface while varying acceleration energy and incident angle. For H atoms, low acceleration energy (0.1 eV) yielded a high probability of reaction with surface Cl to form volatile HCl; this probability decreased as acceleration energy increased. H incorporation into the Nb substrate was most likely at normal incidence (0°) and decreased at higher incident angles. For Ar atoms, $NbCl_4$ desorption was observed when the acceleration energy exceeded 10 eV, whereas surface structural collapse occurred above 100 eV. In contrast to H, Ar showed no strong dependence on incident angle.Experimentally, Nb PE-ALD was performed at 175 °C using an H_2/Ar plasma step with substrate bias. Comparing two bias conditions, (a) 60 W for 7 s and (b) 60 W for 3 s followed by 30 W for 4 s, the lower-bias sequence reduced residual Cl as quantified by XPS from 0.98% (a) to 0.33% (b). The combined simulation/experiment results suggest that suppressing excessive ion energy while maintaining sufficient hydrogen-driven chlorination removal is key to lowering halogen impurities in low-temperature Nb PE-ALD.

2:15pm **AF1-WeA-4 Study of Pd Ald as a Growth Enhancer for Ultrathin CoW Liner/Barrier Layer ALD**, *Noboru Sato, Wataru Mori, Souga Nagai, Yichen Zou, Yuxuan Wu, Yubing Deng, Jun Yamaguchi, Naoki Tamaoki, Atsuhiro Tsukune,* ***Yukihiro Shimogaki***, The University of Tokyo, Japan

Cu interconnects in advanced ULSI employ a bilayer liner/barrier stack to ensure adhesion to Cu and to suppress Cu diffusion. As scaling progresses, however, the effective resistivity of Cu line increases, motivating the use of a single-layer CoW liner/barrier that can provide both adhesion and barrier functions while improving the Cu volume fraction. A major challenge in forming an ultrathin (1–2 nm) continuous CoW film on dielectric surfaces by ALD is the intrinsically low nucleation density of metal ALD on insulators ($<10^{10}$ cm^{-2}), whereas $>10^{14}$ cm^{-2} is typically required for immediate film continuity.

To address this nucleation bottleneck, we explore Pd as a catalytic growth enhancer (GE) for CoW ALD. We previously observed that Co ALD on PVD-

Pd/SiO_2 increases the Co nucleation density to ~10^{12} cm^{-2}, i.e., ~100× higher than conventional nucleation on dielectrics [1]. Building on this concept, the present work aims to develop a Pd ALD process capable of forming Pd clusters with nucleation densities ≥10^{13} cm^{-2} on dielectric surfaces, thereby further enhancing the initial nucleation of CoW.

First, we investigated the chemisorption behavior of the Pd precursor $Pd(hfac)_2$ using neural-network-potential molecular dynamics (NNP-MD). The NNP was trained to reproduce dispersion-corrected PBE (Perdew–Burke–Ernzerhof) reference data using Matlantis™. NNP-MD simulations at 450 K showed no chemisorption of $Pd(hfac)_2$ on hydroxyl-terminated SiO_2, whereas adsorption was observed on hydroxyl-terminated α-Al_2O_3 within 100 ps. These results suggest that creating an Al_2O_3-like hydroxylated surface is essential to enable high-density Pd nucleation on insulating substrates.

Guided by the simulation, we experimentally performed Pd ALD on SiO_2 and Cu substrates after surface modification with trimethylaluminum (TMA) at 145 °C to form an Al_2O_3-like overlayer. We compared (a) no treatment, (b) TMA treatment followed by air oxidation, and (c) TMA treatment followed by H_2O exposure. On SiO_2, Pd uptake increased after surface modification. On Cu, a marked increase in Pd uptake was obtained only for condition (c). The higher effectiveness of (c) over (b) is attributed to differences in Al_2O_3 surface termination; notably, our MD simulations also indicated that $Pd(hfac)_2$ does not adsorb on gibbsite-like Al_2O_3 surfaces. These combined computational/experimental results provide a practical route to engineer dielectric surfaces for high-density Pd nucleation as a growth enhancer toward ultrathin, continuous CoW liner/barrier ALD.

Reference

[1] Deng et al., Advanced Metallization Conference 2025, #4-3, Oct. 9-10, 2025, Toyo (2025).

2:30pm **AF1-WeA-5 Design and Performance of AI Agents Based on Large Language Models Interfacing with an Autonomous Atomic Layer Deposition Tool**, ***Angel Yanguas-Gil***, *Jessica Jones, Sungjoon Kim, Chi Thang Nguyen, Jeffrey Elam,* Argonne National Laboratory

In this work we introduce the design of an atomic layer deposition (ALD) reactor augmented with an AI interface for autonomous materials synthesis. Our modular interface encapsulates the particularities of the hardware behind a Python interface that communicates with the ALD control software via transmission control protocol (TCP). This interface is compatible with model context protocol (MCP) interfaces used in agentic frameworks. To evaluate its performance, we have integrated our tool with a simple AI agent that leverages a large language model to transform user-supplied queries into ALD processes that are then run in our reactor. Our approach uses a JavaScript object notation (JSON) schema to encode ALD processes. Our experimental results show that the AI interface does not impose a significant overhead to our control software, at least within our fastest 10 ms scale. We also carried out a detailed evaluation of the agent performance based on leading models in three types of tasks: basic instruction tasks and process discovery tasks, where the agent is presented with a target material and needs to identify the correct ALD process compatible with the reactor configuration, and process optimization. Despite the simplicity of our agent design, we observed that most of the advanced models excelled at the instruction tasks. However, only recent models such as o1, o3, GPT-5, and Claude Opus 4, with reasoning capabilities, performed well in process discovery tasks. While the results obtained are promising, we identify areas where AI research could help improve the performance of autonomous process discovery and optimization tasks involving atomic layer deposition.

2:45pm **AF1-WeA-6 Generalized Reaction Networks for Atomic Layer Deposition**, ***Simon Elliott***, Schrödinger, Ireland*; Thomas Ludwig,* Schrödinger*; Thomas Hughes, Chloe Luyet,* Schrödinger*; Jacob Gavartin,* Schrödinger, UK

ALD processes are defined in terms of their underlying chemistry, namely self-limiting gas-surface reactions. Much work has been done to determine the reaction mechanism in specific cases, but a general understanding is lacking regarding the criteria for ALD and the resulting limits on growth rates and sticking coefficients. In this work, we develop a generic reaction network for the deposition or etching of metal oxides by ALD or CVD and use microkinetic modelling (MKM) to compute these measurable process characteristics as a function of process parameters. We use ZnO, Al2O3 and HfO2 as illustrative examples that span a range of metal valences and restrict ourselves to water as the co-reagent, though the extension to sulfides or nitrides in similar Bronsted acid-base chemistry would be straightforward. Building on past mechanistic studies, we identify the elementary forward reactions that together comprise the reaction network as (i) precursor/co-reagent adsorption, (ii) ligand or proton exchange, (iii) elimination of protonated ligands as by-products and (iv) densification into solid film. The reverse of each reaction is also included in the reaction network. We streamline the network by omitting linearly dependent reactions. Since these elementary steps convert one surface intermediate into another, the size of the network scales in principle with the square of the number of intermediates. We therefore restrict the number of surface intermediates to the minimum for the number of ligands per precursor and number of protons per water molecule. Activation free energies for each elementary step would typically be computed with DFT, but here our interest is in how the pattern of relative activation energies across the network affects the overall process. Running MKM simulations of multiple pulse-purge cycles, we establish the bounds for ALD versus CVD behavior in terms of the reactivity of individual metals and ligands. The relative kinetics of ligand transfer and proton transfer are found to be the crucial factor.Having used MKM to identify the chemical spaces where ALD is viable, we then derive the corresponding ranges of growth/etch per cycle and sticking coefficients, which are measurable characteristics of the growth/etch process and can be used as inputs to higher-scale simulations. We present the dependence of these characteristics on precursor mass, metal valence, process temperature and pulse pressure.

3:00pm **AF1-WeA-7 Active-Learning PES Exploration: Fast Reaction Discovery in ALD Chemistry**, *Nicolas Onofrio, Nestor Aguirre,* ***Fedor Goumans,*** Software for Chemistry & Materials, Netherlands

Understanding elementary reaction mechanisms of ALD precursors and plasma species is critical to predict nucleation, film microstructure, and process windows. We describe an automated, active-learning workflow that uses a foundation M3GNet interatomic potential to accelerate potential-energy-surface (PES) exploration and discover mechanistic pathways for ALD chemistries. Starting from a compact DFT seed set, the M3GNet model is fine-tuned and used to propose adsorption states, intermediates and transition-state candidates via ML-guided scans and NEB initializations. An uncertainty-aware query policy identifies high-value configurations for targeted DFT verification; verified results are fed back to the MLIP in iterative retraining. This loop expands PES coverage by orders of magnitude for a fixed DFT budget while maintaining DFT-level accuracy for kinetically relevant energetics. Verified elementary steps parameterize kinetic models (kMC) to evaluate nucleation, lateral growth and defect incorporation under varied pulse timing, temperature and co-reactant conditions. In ALD case studies (high-k precursor screening and Ru–H chemistries) the ML-augmented exploration uncovered low-probability dissociative channels and alternate TSs that materially affect predicted growth and electronic proxies. The approach enables faster, physics-grounded mechanism discovery and targeted DFT allocation, shortening precursor screening cycles and providing mechanistic insight for process engineers.

3:15pm **AF1-WeA-8 in-Silico, High-Throughput Exploration of Ald Reaction Mechanisms**, ***Martin Siron***, *Luis Pinto,* Entalpic AI, France*; Tristan Deleu,* Entalpic AI, Canada*; Alexandre Duval,* Entalpic AI, France

Understanding and ultimately controlling the elementary surface reaction steps that govern atomic layer deposition (ALD) remains a fundamental challenge for rational precursor design, growth selectivity, and process optimization. Although ALD is often idealized as a sequence of perfectly self-limiting half-reactions, practical film growth frequently proceeds through a complex interplay of competing ligand-exchange pathways, surface restructuring, precursor fragmentation, parasitic decomposition, and coverage-dependent kinetics. Quantitative prediction of reaction barriers, mechanistic branching, and rate-determining steps is therefore essential to connect molecular-scale surface chemistry with macroscopic deposition behavior such as growth-per-cycle (GPC), conformity, and selectivity.

Recent advances in high-throughput in silico reaction discovery, automated reaction network construction, and machine-learning interatomic potentials (MLIPs) are enabling mechanistically informed exploration of ALD chemistry at unprecedented length and time scales. By combining algorithmic reaction enumeration, accelerated transition-state refinement, and ML-driven reactive sampling, emerging computational frameworks provide a systematic route to map ALD reaction landscapes, identify kinetic

bottlenecks, and evaluate competing pathways across broad precursor–surface chemical spaces.

At Entalpic, we develop agnostic and scalable workflows for the automated construction of complete ALD reaction mechanisms by integrating state-of-the-art cheminformatics and quantum chemistry methodologies. Using bond–electron formalism–based reaction enumeration, we generate comprehensive sets of chemically plausible surface reactions, intermediates, and mechanistic pathways. Thermodynamic screening of reaction networks is rapidly performed using MLIPs, enabling efficient evaluation of large chemical spaces beyond the limits of conventional density functional theory.

To characterize kinetic accessibility, we compute activation barriers through a combination of transition-state sampling strategies, including advanced methods such as Popcornn, alongside generative approaches for transition-state structure proposal and refinement. Through the LeMaterial initiative, we are assembling the largest curated database of transition-metal–organic complex reaction pathways, which directly supports the training of predictive and generative models for mechanistic inference. In parallel, we have benchmarked key elementary reactions for technologically relevant ALD precursors, establishing mechanistic descriptors that correlate with experimentally observed growth-per-cycle trends.

ALD Fundamentals: Growth and Characterization
Room HB Plant Ballroom - Session AF2-WeA
Modeling for ALD Processes II

Moderators: Simon D. Elliott, Schrödinger, **Michael Nolan**, University College Cork

4:00pm **AF2-WeA-11 Validation of the Direct Simulation Monte Carlo Method for the Numerical Modelling of ALD Conformality***, **Paul Nizenkov**, Asim Mirza, Stephen Copplestone, Julian Beyer,* boltzplatz - numerical plasma dynamics GmbH, Germany*; Simone Lauterbach, Marcel Pfeiffer,* Institute of Space Systems, University of Stuttgart, Germany

Atomic layer deposition (ALD) processes span a wide range of length scales and operating pressures, from nano-scale semiconductor features to micrometer-scale structures in MEMS. This means that diffusion processes can range from free molecular flow to the transitional Knudsen regime, where conventional fluid models may require empirical corrections to accurately predict film conformality.

Direct Simulation Monte Carlo (DSMC) offers a reliable approach to the simulation of rarefied gas dynamics on a molecular level. The method has been extensively validated against experimental measurements in different applications including turbo-molecular pumps, spacecraft re-entry aerothermodynamics, and vacuum systems in general. Its ability to accurately resolve gas flow across a wide range of Knudsen numbers, makes it ideally suited for ALD applications spanning multiple flow regimes.

We apply the DSMC method using the open-source plasma simulation framework PICLas to simulate Al_2O_3 ALD conformality from TMA/H_2O in lateral high-aspect-ratio channels. The method is validated against experimental thickness profiles from Arts et al. (2019), then employed to evaluate the extended slope method by Gonsalves et al. (2024) in the transitional regime. DSMC enables seamless multi-scale coupling between reactor-level transport and feature-scale deposition, providing a framework for determining sticking coefficients across industrially relevant conditions. Additionally, PICLas offers the capability to investigate plasma-enhanced ALD processes in the future.

4:15pm **AF2-WeA-12 Multi-Scale Model for Optimization of HfO_2 ALD in High Aspect Ratio Structures***, **Ivan Petras**, Andrey Smirnov, Yury Shustrov,* Semiconductor Technology Research d.o.o. Beograd, Serbia

ALD is characterized by two self-limiting steps and purging. Each step requires a certain time to ensure complete coverage of the surface by precursor and complete removal of excess precursor from reactor volume and surfaces during purging. DRAM capacitors have a complex structure, so it is important to form high-k thin film conformally with excellent step coverage to reduce leakage current. Thus ALD is a key technology for scaling of deep trench DRAM capacitors, where film thickness required is low. HfO2 ALD presents a challenge for conformal deposition in high aspect ratio (HAR) structures due to specific processes such as narrow temperature window due to precursor properties or film quality. In this sense, multi-scale models with coupled reactor- and feature-scale simulations can be applied for reducing process development costs and achieving conformal trench coverage. Focus of this work is aimed at improvement of HfO2 ALD process with consideration of patterned wafers by tuning type of precursor, dosing and purging duration. HfCl4 is known for its thermal stability and ease of use but has the disadvantage of having corrosive by-products, whereas hafnium amides are considered promising due to their high reactivity, non-corrosiveness, and suitability for low temperature processes. An integrated modeling approach was developed with self-consistent coupling of modeling tasks on different scales. Reactor-scale model of Hf-delivery by either HfCl4 or TDMAHf, oxidation and purging include unsteady mass transport with surface chemical reactions. Trench-scale model includes tracing Hf- and oxide precursor species, as well as products of surface chemical reactions.We demonstrate results of process recipe optimization for conformal deposition of HfO2 on patterned wafer within the smallest possible ALD cycle time using multi-scale model. It is shown that optimization of purging is important to keep as few impurities and conformal deposition as possible. Increasing of trench AR leads to remarkably longer time for achieving ALD conformality during precursor delivery, especially for HfCl4 due to secondary effects such as H2O adsorption or etching by HCl by-product. Effect of temperature and H2O purge step duration on resulting film stoichiometry is shown, demonstrating the importance of purge duration due to adsorption of additional H2O. Coating of deep trench surface with each of the precursors has its own characteristics that must be taken into account when optimizing the recipe. Due to its lower reactivity, chloride covers the trench surface more evenly than organometallic precursor. In addition, reactivity of both precursors is sensitive to temperature in different ways. Step coverage dependence on precursor pulse duration is shown for different precursors, pressure and trench AR. Optimal process parameters of HfO2 ALD in HAR trenches are discussed according to temperature range and precursor choice.

4:30pm **AF2-WeA-13 Engineering the Interlayer Materials to Improve Interfacial Thermal Conductance***, **Saikat Mukhopadhyay**,* U.S. Naval Research Laboratory*; Neeraj Nepal, Brian Downey, James Champlain, Shawn Mack, James Lund, Peter Litwin, Virginia Wheeler,* US Naval Research Laboratory

The heterogeneous integration of diverse material components is crucial for developing advanced, multi-functional microelectronic circuits. A significant challenge in this approach is the thermal boundary resistance at material interfaces, which can impede heat dissipation and compromise the performance and reliability of devices. As device sizes shrink and power densities rise, enhancing the interfacial thermal conductance (TBC) has become a critical aspect of thermal management. Recent research on GaN/SiC and AlGaN/Diamond interfaces suggests that introducing an interlayer material can effectively improve TBC.

However, the impact of different interlayer materials and their thickness on TBC is not well understood, and conventional theoretical models like the Acoustic Mismatch Model (AMM) and Diffusion Mismatch Model (DMM) are insufficient as they do not account for the critical role of interfacial states. To address this, our study focuses on the TBC of GaAs/Diamond and GaN/Diamond interfaces, both with and without interlayer materials. We employed advanced transport approaches, including the Non-Equilibrium Green's Function (NEGF) method and Reverse Non-Equilibrium Molecular Dynamics (RNEMD), to accurately calculate TBC incorporating the chemical reconstructions that happen at the interface.

Our calculations find that TBC through GaN/AlN/Diamond is significantly higher than GaN/Diamond. This can be explained in terms of much higher TBC associated with GaN/AlN and AlN/Diamond interfaces compared to the direct GaN/Diamond interface. This motivated a broader investigation using a series of interlayer materials (AlN, TiN, and TaN). We found that all interlayer materials improved the TBC for the GaN/Diamond interface, with TiN yielding the maximum improvement. Additionally, a nearly linear increase in TBC was observed when the TiN layer's thickness was increased from 3nm to 6nm, resulting in a 10% enhancement. Conversely, for the GaAs/Diamond interface, we did not observe a similar improvement in TBC, but the introduction of an AlN interlayer was found to improve the structural stability of the interface. This work provides guidance for future ALD experiments with carefully selected interlayer materials to optimize thermal management in next-generation electronic devices.

4:45pm **AF2-WeA-14 Closing Remarks and Award Presentations***,*

ALD for Manufacturing
Room Tampa Bay Salons 1-2 - Session AM1-WeA

ALD Manufacturing Equipment and Processes

Moderators: Paul Poodt, SparkNano, **Sami Sneck**, Beneq

1:30pm **AM1-WeA-1 Advanced Batch Atomic Layer Deposition Technology for Future 3D Device***, Kazuhiro Harada,* KOKUSAI ELECTRIC CORPORATION, Japan **INVITED**

Semiconductor logic and memory devices are increasingly being structured in three dimensions, leading to a dramatic rise in demand for Batch Thermal Atomic Layer Deposition processes.

In this context, we will discuss the process trends for each type of 3D device (Logic, NAND, DRAM) and the necessity of Batch Thermal ALD technology.

Batch Thermal ALD enables thin film formation on complex 3D devices while maintaining high quality, coverage, and productivity.

Specifically regarding film quality, the extended time available for each ALD step allows for the formation of extremely high-quality films, even in complex three-dimensional structures.

Furthermore, the latest ALD techniques are being deployed in the industry, not only for conformal deposition but also for seamlessly embedding films into complex shapes and for targeting film formation in specific locations.

Gap fill technology requires not only vertical filling but also the challenging horizontal filling without creating seams.

Additionally, applying Area Selective Atomic Layer Deposition technology to silicon dielectric films is essential, particularly around logic Gate-All-Around (GAA) and 3D NAND cells, to simplify complex integration processes, create 3D structures, and enhance device performance.

To achieve these advanced ALD processes, new precursors and process technologies that precisely control termination, bonding states, steric hindrance, and other factors are required.

We look forward to discussing the evolution of our unique Batch Thermal ALD process for 3D devices and exploring the future prospects of the ALD industry with partners from various technical fields.

2:00pm **AM1-WeA-3 On-Demand Precursor Delivery for Atomic Layer Deposition Using Machine Learning-Based Feedforward Control of Piezoelectric Valves***, Kanta Ishida, Hiroshi Nishizato, Shota Oda,* Kumamoto University, Japan*; Yugo Nakaya,* HORIBA STEC, Co., Ltd., Japan*; Kinichi Nasu, Hiroshi Okajima, Takeshi Momose,* Kumamoto University, Japan

We constructed an on-demand precursor/reactant delivery system through precise flow-rate control enabled by piezoelectric valves. With this system, a precursor is flown only during the precursor dosing step, while stopped during the other three steps. To achieve pressure stability and quick switching of gases equivalent to the conventional run/vent system, steep, ideally stepwise, flow rate changes in opening/closing these valves are mandatory rather than slow changes. Therefore, in-house piezoelectric valves, providing fast response and allowing control of opening ratio over time, were developed, and a recipe to control opening ratio over time was then designed using machine learning and control engineering approach, enabling feedforward control of the valves to achieve these operations. It enables a significant reduction in precursor and reactant consumption during ALD.

Wasting precursors across the three steps, except the precursor dosing step, is a critical issue for making ALD processes environmentally sustainable, especially with run/vent delivery systems. The duration of the precursor dosing is typically reported to be only 1–10% of the ALD cycle [1]. It implies that more than 90% of the precursor is discarded to the vacuum pump without contributing to film growth. To address this issue, establishing an on-demand precursor/reactant delivery system is imperative. However, precise flow-rate control has been challenging due to the transient response caused by gas accumulation upstream of the valve during closure, which rushes into the reactor upon opening.

We characterized the piezoelectric valve and identified that hysteresis between the applied voltage and opening ratio, and nonlinear flow responses, are the main factors hindering precise waveform formation, and, thus, challenging precise flow rate control through the following three phases. First, the transfer function from the opening ratio to the flow rate was derived. Second, to compensate for these nonlinearities, we used machine learning to model the valve behavior and design optimal voltage waveforms that overcome hysteresis. Third, we achieved feedforward control based on the developed mathematical model and verified the flow rate. The results demonstrated that the proposed method significantly reduced convergence time to the target flow rate compared with conventional step inputs, resulting in a stepwise gas supply profile.

References [1] O. Graniel *et al.*, *ACS Mater. Au* 3, 296 (2023).

Keywords; On-demand delivery, ALD, Piezoelectric valve, Feedforward control, Sustainability

2:15pm **AM1-WeA-4 Design and Flow Optimization of Additively Manufactured Manifolds for Process/Purge Valves in Atomic Layer Deposition***, Frank Horvat, Ph. D., Ben Olechnowicz, Masroor Malik,* Swagelok Company

Valve manifolds used in Atomic Layer Deposition (ALD) for precursor delivery and system purging are typically fabricated using standard subtractive machining techniques, which impose strict and highly limiting constraints on internal fluid flow-path geometry. As a result, internal flow fields tend to develop recirculating vortical structures, jet impingement at junctions, high pressure losses, and stagnant volumes, adversely affecting precursor uniformity and delivery in the viscous and transitional flow regimes relevant to ALD. In contrast, additive manufacturing enables the development of manifolds with optimized internal geometries, continuous cross-sectional transitions, and reduced junction complexity while keeping the semi standard for surface roughness. Theseoptimized, additive created geometrieseither suppress or reduce flow separation, lower pressure drop, and minimize stagnant regions leading to improved flow conductance, more uniform precursor transport, and enhanced temporal control of precursor dosing in ALD systems.

This poster will show a comparative analysis of conventionally machined versus additively manufactured ALD valve manifold flow-path geometries using computational fluid dynamics (CFD). The results highlight how geometry-enabled flow control reduces pressure loss, suppresses recirculation and stagnation, and improves precursor transport uniformity and temporal response under viscous and transitional flow conditions relevant to ALD processes.

Authors: Frank Horvat, Ph. D., Senior Scientist, Swagelok Company
Ben Olechnowicz, Product Manager - ALD Valves, Swagelok Company
Masroor Malik, Lead Solutions Specialist - Semiconductor, Swagelok Company

2:30pm **AM1-WeA-5 Stability of MoCl5 in Heated Canisters and During Delivery***, Berc Kalanyan, James Maslar,* National Institute of Standards and Technology (NIST)

Molybdenum pentachloride ($MoCl_5$) is an industrially important precursor for applications in atomic layer deposition and etching using fluorine-free chemistry. As a low-volatility solid that is susceptible to hydrolysis, the use of $MoCl_5$ in manufacturing presents significant challenges in mass transport reproducibility and in-situ generation of impurities, including molybdenum oxychlorides, which are also reactive under process conditions. NIST has been developing various optical methods of detecting $MoCl_5$ and MoO_xCl_y with high sensitivity and time resolution. This paper will describe the use of UV-vis and infrared absorption spectroscopies and non-dispersive gas analyzers to evaluate the stability of $MoCl_5$ in canisters and during delivery. Static measurements of the canister headspace in the absence of carrier gas are used to distinguish between trace moisture ingress into the delivery system from finite leaks vs entrainment in the carrier gas. Contributions from the latter moisture source are estimated using a cavity ringdown moisture analyzer installed inline with the carrier gas. The effect of $MoCl_5$ canister temperature, carrier flow rate, idle time, and pulse duration on mass delivery and impurity generation will be presented. Best practices and implications for deposition and etching applications will also be discussed.

2:45pm **AM1-WeA-6 Precursor-Driven Morphology Tuning in ZnO Grown by ALD on 8-Inch Wafers***, Katherine Guzey, Noah Brechmann,* Fraunhofer IMS, Germany*; Thomas Gemming, Marcel Schmickler, Harish Parala,* Leibniz Institute for Solid State and Materials Research, IFW Dresden, Germany*; Anjana Devi,* Fraunhofer IMS; Leibniz Institute for Solid State and Materials Research, IFW Dresden; Dresden University of Technology, TU Dresden, Germany*; Nils Boysen,* Fraunhofer IMS, Germany

As a wide-bandgap semiconductor, thin conformal ZnO films are extensively used as transparent electrodes or sensing layers, as well as in other optoelectronic and microelectronic applications. The most commonly used precursor for industrial-scale ZnO ALD is diethylzinc (DEZ), which is pyrophoric and has a non-ideal ALD window. Recently, Bis(dimethylaminopropyl) zinc(II) ($[Zn(DMP)_2]$) has been introduced, exhibiting non-pyrophoric behavior, higher thermal stability, and sufficient

volatility for ALD at low temperatures. However, this new precursor has been tested only for ALD in small-scale reactors on small substrates.[1,2]

In this study, we investigated and optimized a thermal ALD process for growing ZnO on 8-inch wafers using [$Zn(DMP)_2$] and H_2O as precursors, and compared its performance with the established process using DEZ. Ellipsometry showed that high wafer-scale uniformity was achieved across the entire 8-inch wafer, with 1σ nonuniformities below 1 % at a deposition temperature of 200 °C (Fig. 1a,b). The saturation study for [$Zn(DMP)_2$] (Fig. 1d) confirmed the self-saturating nature of the process for a pulse time of 1.6 s and above, with a more stable growth per cycle of 1.0 Å to 1.1 Å for [$Zn(DMP)_2$], especially at higher temperatures (Fig. 1c). This suggests that the latter precursor is more suitable for deposition temperatures above 200 °C. GI-XRD measurements revealed a polycrystalline hexagonal crystal structure with a dominating (002) reflection in all patterns. The texture along the c-axis is significantly enhanced for ZnO films deposited from [$Zn(DMP)_2$] at higher deposition temperatures.

Analysis by Rutherford backscattering spectrometry (RBS) and X-ray photoelectron spectroscopy (XPS) revealed that highly pure films can be obtained with both precursors within a deposition temperature range of 150 °C to 300 °C. Functional properties were subsequently evaluated by patterning the ZnO films into Van-der-Pauw test structures on 8" wafers to evaluate the sheet resistance(Fig. 3a,b), which was comparable for both precursors (~2200 Ω/sq for [$Zn(DMP)_2$] and ~700 Ω/sq for DEZ). AFM, GD-OES, and TEM (Fig. 3c-f) further confirmed these results.

In summary, the precursor [Zn(DMP)2] provides a viable alternative for the ALD of ZnO on 8-inch wafers, which we demonstrated for the first time. Compared to the established DEZ, processes using [Zn(DMP)2] offer a wider ALD window and a higher crystalline texture along the c-axis, which is highly beneficial for electrical and optical applications. This work therefore paves the way for industrial-scale adoption of the [Zn(DMP)2] precursor and broadens the options for precise parameter control in ALD-grown ZnO.

3:00pm **AM1-WeA-7 Novel Method to Quantify High Surface Area Microloading Effects on Film Conformality**, ***Jussi Kinnunen***, *Kalle Eskelinen,* Chipmetrics Oy, Finland*; Stefan Polzin,* Chipmetrics GmbH, Germany*; Feng Gao, Mikko Utriainen,* Chipmetrics Oy, Finland

As device integration moves toward three-dimensional architectures, atomic layer deposition (ALD) increasingly operates under conditions where extreme aspect ratios coexist with strongly varying local surface area loads. In industrial environments, such variations are known to cause microloading effects, where competition for reactant supply leads to local precursor depletion and reduced effective partial pressure, impacting film uniformity and process window stability [1]. However, the magnitude and spatial extent of these effects between neighboring structures with vastly different surface areas remain difficult to quantify using blanket-based monitors.

In this work, we experimentally quantify microloading-induced conformality loss by combining high surface area (HSA) and high aspect ratio (LHAR) test structures within the same ALD process run. Experiments were performed in a Beneq TFS 200 reactor using thermal Al_2O_3 ALD. PillarHall® LHAR5 chips were processed either alone or placed in close proximity to a VHAR1 chip containing a 15 × 15 mm^2 array of 1 µm diameter, 200 µm deep holes, representing a localized HSA sink. To express the observations in terms of effective reactant supply, the LHAR profiles were analyzed using a Python implementation of the DReaM-ALD diffusion–reaction model [2], based on formulation by Ylilammi et al. [3].

Film conformality was quantified using the penetration depth PD50. Without the VHAR1 HSA structure present, PD50 was 185 µm, corresponding to an effective entrance precursor partial pressure pA0 of 355 Pa. When the LHAR5 chip was placed adjacent to the HSA region, PD50 decreased to 136 µm (195 Pa). At a separation of 5 mm, PD50 recovered to 145 µm (225 Pa), indicating a distance-dependent microloading effect.

The results demonstrate that combining VHAR– and LHAR test structures provide a sensitive and quantitative method to probe microloading effects and local precursor partial pressure variations that remain invisible to blanket wafer measurements. This enables early detection and qualification of layout-dependent conformality risks in mixed-pattern environments, supporting a robust process window definition for high-volume manufacturing.

References

[1] J. Seo et al., Deriving optimal atomic layer deposition process conditions using machine learning,J. Ind. Inf. Integr, Vol 47, 2025, 100879

[2] E. Verkama et al., DReaM-ALD – Diffusion-Reaction Model for Atomic Layer Deposition, (2023), Github, https://github.com/Aalto-Puurunen/dream-ald.

[3] M. Ylilammi et al.. Modeling Growth Kinetics of Thin Films Made by Atomic Layer Deposition in Lateral High-Aspect-Ratio Structures, (2018), J. of Appl. Phys., 123: preprint 205301.

3:15pm **AM1-WeA-8 High–Aspect–Ratio Integrations: A Path to Full Conformality from $HfCl_4$ and Select Oxidizers**, ***Rong Zhao***, *Eric Condo, Bryan Hendrix,* Entegris*; Jimmy Huang,* Entegris, Taiwan

Highly conformal films of HfO_2 by Atomic Layer Deposition (ALD) are critical for future nodes of Complementary Field–Effect Transistor (CFET) logic, advanced high–aspect–ratio (HAR) 3D-NAND flash memory, and future integrated ferroelectric devices. While $HfCl_4$-based ALD processes offer superior electrical performance compared to amide-based precursors, ozone (O_3) as a sole co-reactant results in poor growth per cycle (GPC) and restricted penetration into HAR architectures. In this work, we present a systematic evaluation of alternate oxidizer strategies to overcome the intrinsic limitations of O_3–only processing. The application of mixed O_3 (generated from 20% N_2/O_2 feed gases) and blended O_3+N_2O gases demonstrates significant improvements over baseline, yielding higher GPC, enhanced within wafer (WIW) film uniformity, and increased step coverage on full wafers and test structures with 11:1 aspect ratio (AR). Using optimized conditions at 250–350°C, alternate oxidizer processes achieve near–ideal conformality and uniformity, including ~100% step coverage on 11:1 HAR features, validating their suitability for advanced integration. Postannealing up to 1000 °C confirms film stability, showing negligible shrinkage and consistent refractive index. Film analysis by SIMS supports minimal impurity incorporation indicating clean oxidation pathways and robust compositional control.

Furthermore, Density Functional Theory (DFT) simulations were conducted to investigate adsorption interactions of O_3 and various NO_x species on HfO_2 surfaces. Our studies identified the critical reaction pathway, providing a clear explanation for the improved GPC and step coverage observed with the alternate oxidizers.

Our results establish alternate–oxidizer $HfCl_4$ ALD as a strong candidate for next–generation logic and memory fabrication, offering scalable improvements in uniformity, conformality, and film purity essential for continued vertical device scaling.

ALD for Manufacturing
Room Tampa Bay Salons 1-2 - Session AM2-WeA

Digital Twins for ALD

Moderators: Berc Kalanyan, National Institute of Standards and Technology (NIST), **Pouyan Navabi**, University of Chicago

4:00pm **AM2-WeA-11 Development and Validation of $MoCl_5$ Delivery Simulations: From Canister to Deposition Chamber**, ***James Maslar***, *Vladimir Khromchenko, Berc Kalanyan,* National Institute of Standards and Technology (NIST)

The development of a digital twin for an ALD process could facilitate efficient process development and process control, thereby reducing waste and costs. One approach to the development of such a digital twin is to use computational fluid dynamics (CFD) simulations to inform a model based on artificial intelligence/machine learning (AI/ML). CFD simulations can capture the important physical and chemical processes during ALD but such simulations are too slow to be used even in near real time. AI/ML models have the potential for rapid process simulation and real time process control but need to be trained on a data set that captures the relevant physical and chemical processes. This paper describes the development and validation of CFD simulations of $MoCl_5$ vapor transport in a deposition tool, a first phase of developing an AI/ML DT for $MoCl_5$-based ALD processes. The simulations encompass 1) $MoCl_5$ vapor entrainment into an argon carrier gas in a flow over canister; 2) mass transport through valves and delivery lines; and 3) flow through and out of an ALD chamber. After identifying key physical-chemical properties to describe mass transport, the only adjustable parameters used in the simulations were the canister temperature and argon flow rate. The values of the $MoCl_5$ vapor pressure and $MoCl_5$/argon binary diffusion coefficient are necessary to simulate $MoCl_5$ vapor entrainment in an argon carrier gas and were estimated from temperature-dependent mass carryover measurements. The gas velocity is necessary to simulate flow fields in the chamber and was estimated based

on pressure measurements at different locations in the tool. The simulations were validated using optical absorption measurements to quantify the time-dependent $MoCl_5$ partial pressure at multiple locations in the tool, including in the deposition chamber where absorption imaging was used to visualize $MoCl_5$ flow.

4:15pm **AM2-WeA-12 Achieving Digital Twin in ALD by Combining AI, Computational Chemistry and Experimental Data***, **Luis Pinto**, Martin Siron,* Entalpic, France*; Tristan Deleu,* Entalpic, Canada*; Alexandre Duval,* Entalpic, France

The core challenge in ALD is that growth-per-cycle (GPC) emerges from an interplay between surface chemistry and operating conditions. On one hand, we look at ligand-exchange pathways, parasitic decomposition, nucleation behavior, and temperature-dependent kinetics. On the other, we need reactor geometry, substrate identity, temperature, dosing time and purge time. A high-fidelity digital twin for thermal atomic layer deposition (ALD) would thus not be limited to chemistry, but also incorporate process modelling. It would convert routine metrology and operating logs into predictive capability for process analysis and control, enabling faster recipe development, reduced precursor waste, and improved tool-to-tool reproducibility.

Entalpic is developing such AI-enabled digital twin of thermal ALD reactors, predicting macro-scale deposition outcomes while remaining anchored to mechanistic understanding. The model ingests precursor and co-reactant identity together with key process parameters (substrate, substrate temperature, and timing variables) and outputs GPC with calibrated uncertainty. To improve transferability and interpretability, we standardize experimental context across datasets, incorporate structured representations of reactor delivery behavior, and integrate mechanistically informed descriptors derived from reaction pathways and energetics.

The resulting digital twin supports two complementary capabilities. First, it enables recipe optimization within chemically consistent constraints, identifying conditions that achieve target growth while minimizing excess dosing, exposure time, and process margins. Second, as the dataset expands in chemical and operational diversity, it can generalize toward new precursors by connecting molecular-scale energetics and mechanistic signatures to reactor-scale GPC trends, while signaling when predictions fall outside the model's reliable domain. Models are trained on curated literature deposition reports together with experimental datasets from partners, providing a continuously improving, metrology-aware foundation that links ALD process control with precursor discovery and down-selection, and that can be directly integrated with our internal AI pipeline for precursor discovery to prioritize candidates most likely to deliver robust growth and manufacturable process windows.

4:30pm **AM2-WeA-13 Process Window Engineering for Void-Free STI Gap Filling Using Integrated PEALD and Virtual DOE***, **Wan Yu**, Xiaoxin Li, Pengfei Lyu, Yicheng Xie, Tong Lei, Jian Huang, Yushan Chi,* Lam Research Corporation, China

This study introduces a systematic approach to process window engineering for void-free Shallow Trench Isolation (STI) gap filling using an integrated ALD-Etch-ALD (Atomic Layer Deposition) technique. Unlike conventional multi-tool Deposition-Etch-Deposition (DED) flows, the proposed method consolidates ALD deposition and etching within a single chamber, significantly reducing process complexity, cycle time, and manufacturing cost. To overcome limitations in experimental design due to wafer resource constraints, Virtual Design of Experiments (DOE) combined with SEMulator3D® simulations was employed to replicate STI structures and evaluate key process parameters. Over 3200 virtual experiments were conducted to investigate the influence of deposition-to-etch ratio, chemical etch versus ion etch balance, and incoming trench geometry on gap-fill performance. Results indicate that a higher proportion of ion etching, increased initial deposition thickness, and larger critical dimensions expand the void-free process window. These findings provide mechanistic insights into the interplay between etch anisotropy and trench morphology, offering a scalable and robust solution for advanced technology nodes.

4:45pm **AM2-WeA-14 Closing Remarks and Award Presentations in HB Plant Ballroom***,*

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