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.

[1] Kozen, A. C., ACS Nano 2015, 9, 6, 5884–5892

[2] Kazyak, E., Chem. Mater. 2015, 27, 18, 6457–6462

[3] Otto, S.-K., ACS Appl. Energy Mater. 2021, 4, 11, 12798–12807

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).

References: [1] I. K. Oh et al., IEEE International Interconnect Technology Conference (IITC), 1-3 (2025). [2] S.-Y. Xu et al., Science Advances 1, e1501092 (2023). [3] A. Bedoya-Pinto, ACS Nano 14, 4405-4413 (2020). [4] A. I. Khan, I. K Oh et al., Science 387, 62-67 (2025).

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.

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