

## Atomic Scale Processing Mini-Symposium

### Room 116 - Session AP+EM+PS+TF-MoM

#### Area Selective Deposition (ASD) I

**Moderators:** Eric Joseph, IBM T.J. Watson Research Center, **Adrie Mackus**, Eindhoven University, Netherlands

#### 8:15am AP+EM+PS+TF-MoM-1 Unlocking the Atomic Canvas: Applications and Challenges of Area Selective Deposition in Next-Generation Memory Devices, *Ebony Mays*, Micron Technology **INVITED**

The semiconductor industry is on the cusp of an AI-driven revolution, propelling scaling and density trends for integrated circuit devices. As we delve deeper into a 3D transformation in circuit architecture, we are driven to find solutions to memory and storage bottlenecks and capacity demands. This necessity is fueling a new wave of architectural, material, and process technology innovations that meet power, performance, and cost demands. The push to control material deposition and removal at the atomic scale over extremely high aspect ratios is more critical than ever. In this context, area selective deposition (ASD) emerges as a powerful tool to meet these evolving challenges. With the application of new materials at higher aspect ratios, we must continue to expand our toolbox with new precursor and deposition technologies for ASD. This talk will address some of the ensuing challenges and hurdles for the use of ASD in manufacturing applications for memory devices. It will also highlight opportunities for innovation and collaboration in these areas, emphasizing the need for future technology innovation. The future of the semiconductor industry hinges on our ability to innovate and collaborate in these critical areas.

#### 8:45am AP+EM+PS+TF-MoM-3 Area-Selective Atomic Layer Deposition by Sputter Yield Amplification, *Arthur de Jong, M. Bär, M. Merckx, E. Kessels, A. Mackus*, Eindhoven University of Technology, Netherlands

Area-selective deposition (ASD) is an emerging technique in device fabrication that can bypass lithography-based fabrication of certain layers in a device stack that require perfect alignment. The distinction between growth and non-growth areas is commonly attained through chemical differences, such as selective precursor or inhibitor adsorption [1]. To expand the ASD toolbox, this study explores a physical approach that integrates (non-selective) atomic layer deposition (ALD) with area-selective sputter etching by ions of the undesired material deposited on the non-growth area. Sputter yield amplification occurs if a non-growth area contains an element with significantly larger mass than the incoming ion [2]. When an ion collides with such atom, the momentum is more effectively redirected upward compared to a collision with a lighter atom. This enhanced redirection augments the energy transfer to the deposited material on the non-growth area, thereby increasing the likelihood of etching. Conversely, the growth area should lack heavy elements, resulting in a considerably lower etch rate of the film that is deposited on top.

Selective sputter etching was investigated for SiO<sub>2</sub> and TiN films. On various substrates, a thin SiO<sub>2</sub> overlayer deposited by ALD was exposed to low-energy Ar ions (33-50 eV). The amount of SiO<sub>2</sub> removed depends significantly on the substrate (Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, Nb<sub>2</sub>O<sub>5</sub>, MoO<sub>3</sub>, HfO<sub>2</sub>, Ta<sub>2</sub>O<sub>5</sub>, and WO<sub>3</sub> were investigated here). In general, the heavier the mass of the metal atoms in the substrate, the less SiO<sub>2</sub> is observed after the ion exposure. TiN was selectively deposited on Al<sub>2</sub>O<sub>3</sub> with respect to a HfO<sub>2</sub> non-growth area by repeating supercycles of six TiN ALD cycles and Ar ion exposure from a plasma. Approximately 7.0 nm of selective growth is achieved on Al<sub>2</sub>O<sub>3</sub> with only 0.15 nm on HfO<sub>2</sub> (giving 96% selectivity). The key benefit of (selective) sputter etching lies in its relative insensitivity to temperature and ALD chemistry. This proof-of-concept shows that exploiting sputter yield amplification can enable ASD processes that are complementary to the existing chemical approaches.

[1] A. J. M. Mackus et al., *Chemistry of Materials* 31, 2 (2019).

[2] S. Berg et al., *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films* 10, 1592 (1992).

#### 9:00am AP+EM+PS+TF-MoM-4 Effectiveness of SiO<sub>2</sub> Functionalization with Methyl versus Silyl Groups to Enable Area-Selective Atomic Layer Deposition of Al<sub>2</sub>O<sub>3</sub>, *Andrew Kaye*, Colorado School of Mines; *S. Agarwal*, Colorado School of Mines, USA; *H. Chandra, R. Pearlstein, X. Lei, A. Derecskei*, EMD Electronics, USA; *B. Zope*, Intermolecular, Inc.

Plasma-deposited SiO<sub>2</sub> films are extensively used in semiconductor manufacturing. Area-selective atomic layer deposition (AS-ALD) of a dielectric, such as Al<sub>2</sub>O<sub>3</sub>, on a target surface with SiO<sub>2</sub> as a non-growth surface, can simplify device processing. Gas-phase functionalization of SiO<sub>2</sub>

using aminosilanes as small molecule inhibitors has been previously reported. Most studies show that growth nucleation during ALD occurs on the functionalized SiO<sub>2</sub> surface after just a few nanometers of deposition on the growth surface. It is speculated that nucleation on the SiO<sub>2</sub> surface occurs due to the availability of unreacted surface –SiOH groups. We tested this hypothesis by functionalizing the SiO<sub>2</sub> surfaces with different densities of surface –SiOH groups with two aminosilanes that offer a different degree of steric hindrance. Specifically, we functionalized of the plasma-deposited SiO<sub>2</sub> surface with N,N-dimethylaminotrimethylsilane (DMATMS) and di-sec-butylaminosilane (DSBAS). *In situ* infrared spectroscopy shows that DMATMS and DSBAS react with isolated surface –SiOH groups resulting in –Si(CH<sub>3</sub>)<sub>3</sub> and –SiH<sub>3</sub> terminated surfaces, respectively. Due to steric hindrance from the bulky di-sec-butylamino ligand, ~50% of the surface –SiOH groups remained unreacted after functionalization of the as-deposited SiO<sub>2</sub> surface: these –SiOH groups became available for reaction with dimethylaluminum isopropoxide (DMAI) during Al<sub>2</sub>O<sub>3</sub> ALD. In contrast, *in situ* 4-wavelength ellipsometry shows that functionalization of the as-deposited SiO<sub>2</sub> surface with DMATMS resulted in a nucleation delay of ~20 ALD cycles due to the much higher surface ligand coverage, which we attribute to a much smaller reactive leaving group. Next, we pre-annealed the as-deposited SiO<sub>2</sub> films at 500 °C, which lowered the surface –SiOH density by ~72%. After annealing, both inhibitors had nearly equal surface coverage, and reacted with most of the available surface –SiOH groups. However, surface functionalization with DMATMS still provided a nucleation delay of ~20 ALD cycles, while DSBAS did not provide any nucleation delay. On the pre-annealed surface, both DMAI and H<sub>2</sub>O did not react with surface –SiH<sub>3</sub> or –Si(CH<sub>3</sub>)<sub>3</sub> groups. Instead, we show that DMAI can strongly absorb onto surface Si–O–Si sites to initiate film growth. Since DMATMS provides a higher degree of steric blocking due to the bulkier –Si(CH<sub>3</sub>)<sub>3</sub> ligand, there is still a nucleation delay on the pre-annealed SiO<sub>2</sub> surface even though the surface density of the ligands is much lower compared to the as-deposited surface.

#### 9:15am AP+EM+PS+TF-MoM-5 Progress Towards a New Class of Area Selective Deposition Using Photoassisted Chemical Vapor Deposition on Thermally Sensitive Substrates, *B. Das, R. Rashmi*, University of Florida; *B. Salazar, C. Brewer*, University of Texas at Dallas; *L. McElwee-White*, University of Florida; *Amy Walker*, University of Texas at Dallas

Area selective deposition (ASD) has been successfully realized in microelectronics using high-temperature processes, but continued performance and scaling, new materials, and future device fabrication schemes require new low-temperature (<400 °C) ASD methods for metals, dielectrics and other films. In this talk we describe progress towards a new low (near room) temperature ASD method in which reactive functionalized self-assembled monolayers direct Ru film deposition using novel photoassisted chemical vapor deposition (PACVD) processes. The ideal precursor for photoassisted low temperature CVD is a volatile complex with a high quantum yield for ligand loss, which provides an empty coordination site for surface attachment. The surface-bound primary photoproduct then undergoes facile decomposition to the target material and for ASD selectively reacts with the functionalized SAM terminal groups. Our initial proof-of-concept studies employed (η<sup>3</sup>-allyl)Ru(CO)<sub>3</sub>X (X = Cl, Br, I) precursors. Three SAMs were employed with –CH<sub>3</sub>, –OH or –COOH terminal groups. Under UV light using (η<sup>3</sup>-allyl)Ru(CO)<sub>3</sub>Br we showed that Ru(0) and RuO<sub>x</sub> selectively deposits on –CH<sub>3</sub> and –OH terminated SAMs but not on –COOH terminated SAMs. We attribute this behavior to the formation of Ru-carboxylate complexes which block deposition. We further show that using (η<sup>3</sup>-allyl)Ru(CO)<sub>3</sub>X (X = Cl, I) precursors only lead to molecular deposition and DFT calculations indicate that this is not due to the primary photoprocess but the energy required to lose a second carbonyl. Most recently we have studied a series of (η<sup>4</sup>-diene)Ru(CO)<sub>3</sub> (diene = butadiene, isoprene, 1,3-cyclohexadiene or cyclobutadiene) to further investigate the role of polyhapto carbon ligands and the metal oxidation state. We have already demonstrated that these complexes undergo photochemical loss of CO and/or the diene and that exhaustive photolysis of the complexes in solution leads to the formation of colloidal Ru. In agreement with our observations using (η<sup>3</sup>-allyl)Ru(CO)<sub>3</sub>Br we show that the primary photoprocess and the metal oxidation state are not the most important reaction variable for Ru metal deposition but rather the energy required to lose further ligands. Further we show that Ru selectively deposits on –COOH terminated SAMs and not on –CH<sub>3</sub> and –OH terminated SAMs.

9:30am **AP+EM+PS+TF-MoM-6 Atomic and Molecular Monolayers on Silicon as Resists for Area-Selective Deposition**, *Andrew Teplyakov*, University of Delaware

As the size of the components in electronic devices decreases, new approaches and chemical modification schemes are needed to produce nanometer-size features with bottom-up manufacturing. Atomic and molecular layers can be used as effective resists to block the growth of materials on non-growth substrates in area-selective deposition methods. However, in order for these monolayers to be useful, it is imperative to know the initial structure and reactivity of these modified surfaces and also to understand what happens when the selectivity is lost. This talk will summarize recent developments in our search for effective resists based on chlorination and bromination of silicon surfaces performed by solution and gas-phase modification methods and preparation of organic monolayers starting with these surfaces. The structure, stability, and reactivity of the modified surfaces will be evaluated with spectroscopic and microscopic techniques, and their performance as potential resists in ALD of titanium dioxide will be discussed. The TiO<sub>2</sub> deposition is performed using thermal ALD with tetrakisdimethylamidotitanium (TDMAT) or TiCl<sub>4</sub> as the source of titanium and water as the co-reactant. The selectivity of the process will be compared to that of unmodified (oxidized) silicon surfaces (prototypical growth surface) and of the H-covered silicon surfaces (prototypical non-growth surface).

9:45am **AP+EM+PS+TF-MoM-7 Selective Deposition of Low k SiCOH and Surface Sialylation Repair of Low K Dielectrics for Nano Cu Interconnects**, *Son Nguyen, H. Shobha, A. Jog, H. Huang, B. Peethala, J. Li, J. Demarest, Y. Yao*, IBM Research Division, Albany, NY

In this paper, we demonstrate the integrated surface sialylation, low-k repair, and selective SiCOH deposition on 32 nm pitch Cu-SiCOH damascene structures to form a 5-6 nm raised SiCOH for the Fully Aligned Via (FAV) integration. Initially, the nominally damaged patterned SiCOH dielectric surface was repaired by UV sialylation process with carbonsiloxane to reduce the typical RIE patterning damage and cyclic selective deposition of Cobalt [4] by replenishing the surface carbon with UV/Thermal assisted carbonsilane precursor repair. The time-of-flight secondary ion mass spectrometry (ToF SIMS) analysis indicates nominal amount of carbon replenished on the SiCOH surface (see Figure 2). This surface sialylation repair reduces the capacitance and significantly improves the TDDB as shown in Figure 1. FTIR analysis also indicates an increased Si-CH<sub>3</sub> bonding in SiCOH surface after sialylation suggesting the replenishment of carbon on the SiCOH surface. After the initial one cycle SiCOH surface sialylation repair with Carbo-Siloxane precursor, additional selective SiC(O) films were deposited using multi step cyclic deposition and treatment processing steps as illustrated in Figure 3. The average selective deposition/H<sub>2</sub> plasma treatment steps per each cycle is about 6A. Electrical measurement on blanket MIS wafers yields a  $k = 4.1 \pm 0.1$  for the selective SiCO layer which is 1.8 times lower compared to selectively deposited of AlO<sub>x</sub> with  $k \sim 7.5$  for FAV applications [2-3]. Figure 4 shows the various analyses for sialylation and SiC(O) selective deposition on SiCOH\_Co capped Cu patterned surface. Clearly, sialylation repair penetrates to SiCOH and selective growth of 6 nm SiC(O) after cyclic processing steps. Figure 5 shows representative image of 32/36 nm pitch FAV structure fabricated after integrated sialylation and selective deposition of 4 nm SiC(O) with UV/Thermal Assisted Vapor Processing. Overall, the integrated Sialylation and selective provide a simpler the low k SiCOH dielectric repairs and selective dep of lower k SiC(O) dielectrics film for FAV and other planar surface applications in electronic device fabrication without the need of SAM that normally required in selective deposition.

## REFERENCES

- [1] B. D. Briggs et al., "IEDM Tech. Dig., Dec. 2017 pp. 338-341
- [2] S. Van Nguyen et al., "Proc. IEEE Int. Interconnect Technol. Conf., paper S7-4, Jul. 2021 Kyoto, Japan.
- [3] H.P. Chen, et al., International Electron Device Meeting 2021, paper 22.1, San Francisco, CA, USA
- [4] C.C. Yang, B. Li, H. Shobha, S. Nguyen, A. Grill, J. Aubuchon, M. Shek and D. Edelstein. IEEE Electron Device Letter, Vol 33, No. 4, pp.588-560 (2012).

\* Figures 1-5 are in supplement

10:30am **AP+EM+PS+TF-MoM-10 Selectivity Loss During Area-Selective Deposition Processes: The Role of Chemical Passivation and Steric Shielding**, *M. Merckx, P. Yu, I. Tezsevin, A. Mackus*, Eindhoven University of Technology, Dept. Applied Physics, Netherlands; *Tania E. Sandoval*<sup>1</sup>, Universidad Técnica Federico Santa María, Dept. Chemical and Environmental Engineering, Chile

INVITED

Area-selective deposition (ASD) processes have been an extensive area of research for the past few decades. Strategies to achieve selectivity include the use of self-assembled monolayers, inherent selectivity of precursor molecules, and most recently, the use of small molecule inhibitors (SMIs). All these different approaches require a fundamental understanding of the mechanism at every step of the process, and more importantly, what determines selectivity loss. In the case of SMIs, there are several challenges related to their vapor phase dosing to be overcome to improve selectivity, such as, reaching high packing, chemical passivation, and steric shielding.[1-2]

This study explores the connection between chemical passivation and steric shielding with selectivity loss using SMIs. Specifically, how the adsorption of the SMI acetylacetone influences the nucleation of trimethylaluminum (TMA), dimethylaluminum isopropoxide (DMAI), and tris(dimethylamino)aluminum (TDMAA) on the non-growth area through displacement reactions.

Through a combination of experimental and theoretical characterization, we found that the observed changes to the non-growth area during ASD are related to the reactivity of the precursor towards the inhibition layer. Infrared spectroscopy reveals that 23% of TMA adsorbs on the non-growth area after SMI adsorption, exceeding DMAI and TDMAA by more than an order of magnitude. Density functional theory calculations are used to explore the role of chemical passivation by calculating adsorption energies of SMI and precursor, as well as displacement energies. We found that differences in reactivity across precursors and SMI are an important metric to determine displacement.

In addition, we carried out molecular dynamics to characterize the role of steric shielding by looking at the inertness of the non-growth area after SMI adsorption, and the different pathways of the precursor to reach the surface. These results show that the adsorption configurations of acetylacetone provide different degrees of steric shielding, where the most weakly adduct promotes precursor adsorption.[3] Moreover, they also show how the small size of TMA is detrimental to blocking as it can easily reach the surface, while TDMAA is more hindered from adsorption. Overall, this study provides important insights into the mechanism for selectivity loss, and highlights the different contributions to precursor blocking, providing a thorough understanding of inhibition in ASD processes.

[1] J. Li, et al. J. Vac. Sci. Technol. A 40, 062409, 2022

[2] P. Yu, et al. Appl. Surf. Sci. J.apsusc.2024.160141, 2024

[3] M.J.M. Merckx, et al. Chem. Matter. 32, 3335-3345, 2020

11:00am **AP+EM+PS+TF-MoM-12 Computational Screening of Small Molecule Inhibitor Candidates for Area-Selective Atomic Layer Deposition**, *Joost Maas, I. Tezsevin, P. Yu, M. Merckx*, TU / Eindhoven, Netherlands; *T. Sandoval*, Universidad Técnica Federico Santa María, Chile; *A. Mackus*, TU / Eindhoven, Netherlands

Area-selective atomic layer deposition using small molecule inhibitors (SMIs) represents a promising avenue to facilitate the downscaling of nanoelectronics. SMIs eliminate challenges such as alignment errors by enabling bottom-up selective growth using vapor-phase processing. Two main factors play a role in the viability of SMI candidates: (i) the inhibitor molecules must adsorb strongly and selectively on the non-growth area and (ii) these molecules must pack densely once adsorbed. In this contribution, these two factors are investigated using density functional theory (DFT) and random sequential adsorption (RSA) simulations respectively.<sup>1</sup> RSA simulations mimic the adsorption of molecules as they arrive one-by-one in gas-phase and are used to determine the chemical passivation (by means of coverage and surface density) and steric shielding (by means of the fraction of covered area) performance of the SMIs.<sup>2</sup> RSA is computationally lightweight and easily scalable.

A four tier simulation approach is followed to screen SMI candidates: (1) DFT on small clusters to determine whether adsorption is energetically favorable and to determine the adsorption configuration. The adsorption configuration is then used to create a 2D footprint of the molecule, such that it can be used in (2) initial RSA simulations of the candidate SMIs,

<sup>1</sup> AVS Rising Star

yielding the coverage and fraction of covered area. (3) Based on this initial screening, the most promising candidates are further tested using periodic DFT to improve the accuracy of our approximation, and (4) RSA is re-run using the updated geometry. By narrowing down the list of candidates within each step, time is spent more efficiently on more complex simulations. A list of 30+ candidates is screened for  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{AlN}$ , and  $\text{Si}_3\text{N}_4$  using this method; surfaces chosen for their applications in semiconductor industry ( $\text{AlN}$  was included for a comparison between oxides and nitrides). The list of candidates is comprised of carboxylic acids and diketones, a selection inspired on the experimental performance of (among others) Hacac and acetic acid. Further divisions are made to investigate the effect of the carbon chain length (up to 5 for valeric acid), halides in the SMI, and reactive atoms (O/N/S). In line with simulation results, experimental results indicate that acetic acid performs well as an SMI, lending credence to the screening approach. Our analysis suggests that formic acid, acetamide, valeric acid, acetamidine, and imidodicarbonic diamide are promising candidates to be used as SMIs for ASD processes.

1. J. Li; et. al. *JVST A* **2022**, 40 (6), 062409
2. Mameli, A.; et. al. *ACS Nano* **2017**, 11 (9), 9303–9311.

**11:15am AP+EM+PS+TF-MoM-13 Ordering of Small Molecule Inhibitors to Block Precursor Adsorption on Cu During Area-Selective Atomic Layer Deposition: A Computational Study, Ilker Tezsevin, J. Maas, M. Merx, Eindhoven University of Technology, Netherlands; S. Semproni, J. Chen, Intel Corporation; T. Sandoval, Universidad Técnica Federico Santa María, Chile; A. Mackus, Eindhoven University of Technology, Netherlands**

Thanks to their industrial compatibility, small molecule inhibitors (SMIs) offer a promising route for achieving area-selective atomic layer deposition (ASALD) in semiconductor fabrication. Cu is widely used in integrated circuits as an interconnect material and is a target non-growth area for many ASD applications. This study explores the adsorption and packing of SMIs on the Cu surface to achieve ASALD considering Cu as the non-growth area.

SMIs are dosed in the vapor phase and arrive one-by-one on random surface sites. Therefore, SMIs typically cannot form a dense ordered layer, leaving some surface sites uncovered and available for precursor adsorption.<sup>1,2</sup> To promote the packing on the surface, an SMI favoring lateral interactions and surface mobility on the non-growth area is required such that a self-assembled monolayer (SAM)-like packing can be achieved. Our screening for effective SMIs using density functional theory (DFT) calculations led to the discovery of the great potential of pyridazine ( $\text{C}_4\text{H}_4\text{N}_2$ ), which exhibits strong adsorption on Cu via its nitrogen atoms. Random sequential adsorption simulations<sup>3</sup> of pyridazine on Cu show that it can densely pack on the surface with a surface density of more than 2.4 molecules per  $\text{nm}^2$  such that precursors with a radius larger than 0.3 nm cannot reach the surface. Furthermore, detailed DFT and molecular dynamics studies suggest that pyridazine molecules show ordering on the Cu surface. Due to its unique adsorption configuration, pyridazine molecules favor lateral interactions resulting in a SAM-like ordering. Additionally, the pyridazine adsorption configuration allows for diffusion or rotation of the inhibitor on Cu with an activation barrier of less than 0.22 eV, enabling denser packing on the surface. In summary, the pyridazine molecule exhibits exceptional adsorption energetics on the Cu surface promoting a densified inhibitor layer on the non-growth area. Hence the unique properties of pyridazine may bridge the gap between the industrial applicability of SMIs and the efficiency of SAMs, making it a promising candidate for ASALD applications targeting Cu non-growth areas.

- (1) Merx, M. J. M.; et. al. *Chem. Mater.* **2020**, 32 (18), 7788–7795.
- (2) Tezsevin, I.; et. al. *Langmuir* **2023**, 39 (12), 4265–4273.
- (3) Li, J.; et. al. *J. Vac. Sci. Technol. A* **2022**, 40 (6), 062409.

**11:30am AP+EM+PS+TF-MoM-14 Revealing the Mechanisms for Loss of Selectivity in Area-Selective ALD Using in-Situ Infrared Spectroscopy, Eric H. K. Wong, M. Merx, J. Maas, I. Tezsevin, W. Kessels, Eindhoven University of Technology, The Netherlands; T. Sandoval, Universidad Técnica Federico Santa María, Chile; A. Mackus, Eindhoven University of Technology, The Netherlands**

To fulfil the needs for self-aligned fabrication in sub-5 nm technology nodes in nanoelectronics, much research efforts have been devoted to the development of area-selective atomic layer deposition (AS-ALD). The use of small-molecule inhibitors (SMIs) is considered to be an industrially-

compatible option due to its vapor-phase dosing. Our previous works have provided mechanistic insights into the first cycle of AS-ALD of  $\text{SiO}_2$  as a model system for understanding blocking by SMIs [1, 2]. However, the mechanisms for loss of selectivity in AS-ALD remain unexplored which is critical to improving the selectivity. In this work, we performed in-situ reflection-absorption infrared spectroscopy (RAIRS) measurements as a function of the number of cycles to reveal the mechanisms of the selectivity loss.

Twenty cycles of an ABDC-type process [3] comprising an acetylacetone (Hacac) inhibitor dose (step A), a bis(diethylamino)silane (BDEAS) precursor dose (step B), and subsequently two plasma ( $\text{H}_2$  and  $\text{O}_2$ ) exposure (steps D and C) were carried out on the non-growth area  $\text{Al}_2\text{O}_3$ . RAIRS spectra were taken after the steps A, B, and DC. We learned in previous work that the adsorption of Hacac on  $\text{Al}_2\text{O}_3$  results in a mixture of chelate and monodentate adsorption configurations, with the chelate configuration being the effective form for precursor blocking [2]. Our results from the current study indicate that the precursor-blocking by the inhibitor layer decreases as a function of cycles. In addition, the mixture of inhibitor adsorption configuration changes to a higher chelate-to-monodentate ratio. DFT calculations indicate that the  $\text{SiO}_2$  defects formed due to the partial loss of selectivity prevent the successful re-application of the inhibitor molecules in the subsequent cycles. In summary, our results suggest that the change of chemical character of the non-growth area due to the formation of defects escalates the loss of selectivity. Furthermore, this work demonstrates a general approach for inspecting the mechanisms for loss of selectivity that can be extended to other AS-ALD systems.

- [1] A. Mameli et al., *ACS Nano*. **11**, 9303–9311 (2017).
- [2] M. J. M. Merx et al., *Chem. Mater.* **32**, 3335–3345 (2020).
- [3] M. J. M. Merx et al., *Journal of Vacuum Science & Technology A*. **39**, 012402 (2020).

**11:45am AP+EM+PS+TF-MoM-15 Use of Sulfide Inhibitors for Multi-Surface Passivation and Area Selective Deposition, Summal Zoha, B. Gu, Incheon National University, Republic of Korea; F. Pieck, R. Tonner Zeck, Leipzig University, Germany; H. Lee, Incheon National University, Republic of Korea**

In recent years, the area-selective atomic layer deposition (AS-ALD) process has excelled over conventional methods for precise and area-selective thin film deposition. This area selective deposition (ASD) method has displayed promising capability for 2D and 3D nanoscale patterning. With the help of inhibitor molecules capable of tailoring the surface properties, thin films can be deposited only on desired growth surfaces using AS-ALD without any unwanted growth on non-growth surfaces. In this regard, small molecule inhibitors (SMIs) have recently gained a lot of attention for their inhibiting capabilities despite having small sizes. The choice of surface inhibitor is crucial in determining the growth, non-growth surface, and the degree of surface passivation. In this study, three organosulfide inhibitors have been utilized for AS-ALD on metal, oxide, and nitride surfaces, Cu,  $\text{SiO}_2$ , and TiN, respectively. These inhibitors display selective adsorption on the Cu surface and in some cases on the  $\text{SiO}_2$  surface, while the TiN surface remains unaffected by the inhibitors. The density functional theory (DFT) study revealed that the inhibitors are capable of decomposing to assist the adsorption of their constituents on the Cu and  $\text{SiO}_2$  substrates, thereby simultaneously inhibiting two surfaces through a single inhibitor. A comparison between the organosulfide inhibitors was performed to comprehend blocking behavior. Blocking results of  $\text{HfO}_2$  ALD revealed that the longer straight-chained organosulfide inhibitor was able to uphold better blocking properties than compared to the shorter and branched organosulfide inhibitor. This concept of multi-surface inhibition by a single inhibitor can be an essential approach for Si device fabrication where several surfaces are exposed under AS-ALD processes.

# Monday Afternoon, November 4, 2024

## Atomic Scale Processing Mini-Symposium

### Room 116 - Session AP1+EM+PS+TF-MoA

#### Area Selective Deposition (ASD) II

**Moderators:** Satoshi Hamaguchi, Osaka University, Japan, Richard Vanfleet, Brigham Young University

2:30pm **AP1+EM+PS+TF-MoA-5 Area Selective Deposition: Advances, Challenges and Future Technology Enablement, Kandabara Tapily, J. Smith, A. deVilliers, G. Leusink**, TEL Technology Center, America, LLC INVITED K. Tapily, J. Smith, A. deVilliers, G. Leusink

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To achieve higher performance, higher density, and lower cost, for decades the semiconductor industry has relied on aggressive scaling of the device feature size using top-down lithography. Additionally, scaling is driving the need for new materials introduction, new processes and new device architectures increasing the integration complexity. As a result, the industry has introduced several scaling boosters such as high  $k$  / metal gate, stress engineering, air gaps and recently area selective deposition to meet the power performance area cost or PPAC requirement.

Advanced device architectures such as gate-all-around (GAA) and complimentary field-effective transistors (CFET) require additional design / technology co-optimized (DTCO) solutions to continue the device scaling roadmap. Selective deposition of materials is fundamental not only for the reduced cost and complexity of manufacturing these advanced devices, but also as fundamental solutions to promote power / performance / CPP scaling of these advanced device architectures.

Surface engineering is key in successfully realizing defect free area selective deposition. Surface sensitive and reaction driven processes such as atomic layer processes (deposition and etch) will be key enabler in some of the required selective deposition processes (1).

This talk will discuss the status and approaches of area selective deposition technology and challenges the industry is facing in implementing future technology nodes. We will go over multiple examples of how novel selective deposition processes can accelerate the industry roadmap in terms of PPAC scaling.

References:

1. G. N Parsons, R. D Clark, *Chem. Mater.*, 32(12), 4920 (2020).

3:00pm **AP1+EM+PS+TF-MoA-7 Examining UV-Induced Functional Group Formation on 2D Nanomaterials for Patterned ALD, Azeez O. Musa, A. Werbrouck, N. Paranamana, M. Maschmann, M. Young**, University of Missouri-Columbia

In our previous work, we employed a focused electron beam (e-beam) within an environmental scanning electron microscope (eSEM) to break down water vapor, allowing for the precise creation of hydroxylated patterns on highly oriented pyrolytic graphite (HOPG) surfaces. These patterns facilitated subsequent atomic layer deposition (ALD) in patterned areas, offering exceptional control over spatial resolution (exceeding 42 nm), and surface selectivity (ranging from 69.9% to 99.7%). However, despite its precision, the use of an e-beam is time-consuming and lacks industrial scalability due to the limited functionalization area on the substrate. In this study, we aim to explore the feasibility of patterning large areas of 2D material using UV irradiation in the presence of water vapor. Specifically, we seek to understand the impact of the direct UV ionization of water vs. ionization of water from secondary emitted electrons. Our experimental setup utilizes a custom-built hot-walled viscous-flow ALD reactor equipped with a vacuum ultraviolet (VUV) source unit with a peak emitted wavelength of 160 nm. This UV source incorporates a compact deuterium lamp with a MgF<sub>2</sub> window and UV photons are focused onto the sample using a convex MgF<sub>2</sub> lens to enhance photon flux density. We posit that the UV irradiation induces the formation of hydroxyl defects on the HOPG surface. To verify this, we employ spectroscopy including X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FTIR), and Raman spectroscopy (RS), assessing the formation of functional groups on 2D material surfaces. We also examine the impact of UV-functionalization on ALD nucleation and growth onto 2D materials. Our studies inform the applicability of this method for patterned thin-film deposition for semiconductor manufacturing.

3:15pm **AP1+EM+PS+TF-MoA-8 ASD of Low Temperature Cu Capping Layers for Polymers-Based 3D Technologies, Silvia Armini**, IMEC Belgium; A. Brady Boyd, Aberystwyth University, UK; E. Chery, IMEC Belgium

With the constant increase of complexity in integrated systems, more and more connections are required between adjacent chips. Advanced packaging technologies using heterogeneous integration rely heavily on the interconnects redistribution layer (RDL) for this routing.

The most promising option to further reduce the interconnect dimensions relies on a dual-damascene process using photo-sensitive polymers as dielectric.

Unfortunately, using a polymer as a dielectric presents serious reliability challenges as polymers are generally unable to block the diffusion of oxygen, resulting in copper oxidation even at temperatures below 200 °C. Additionally, copper oxidation is not self-limiting.

As the critical dimensions of the lines are scaled down, high rates of oxidation are therefore a major reliability concern.

Recently the possibility of protecting the copper lines from oxidation through very thin ALD layers was demonstrated. For example, HfO<sub>2</sub> films as thin as 9 nm have been shown to effectively prevent copper oxidation during aggressive corrosion stress tests. Nevertheless, despite their minimal thickness, these dense films, deposited on the full surface of the wafer, are known to lead to mechanical stress. Ultimately, this stress can result in delamination and fracture during the next process steps.

To overcome this issue, area-selective deposition of TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> capping layers on Cu with respect to polymers are studied and their reliability performance investigated

3:30pm **AP1+EM+PS+TF-MoA-9 SiO<sub>2</sub> Fluorination/Passivation for Area-Selective Deposition of TiO<sub>2</sub>, ZnO, and Polymer on Metal and SiN<sub>x</sub> vs. SiO<sub>2</sub>, Jeremy Thelven, H. Oh, H. Margavio, G. Parsons**, North Carolina State University

Challenges related to nanoscale pattern alignment are motivating research in chemically-directed patterning by Area-Selective Deposition (ASD) for future 3D devices. Recently, we have begun to explore the growth and inhibition mechanisms of metal oxide ALD materials (Al<sub>2</sub>O<sub>3</sub>, ZnO, and TiO<sub>2</sub>) on hydroxylated and fluorinated SiO<sub>2</sub>, and hydroxylated and fluorinated silicon nitride, SiN<sub>x</sub>. The ability to selectively react and deposit on an oxide vs nitride surface is recognized as a key problem due to the wide use of SiO<sub>2</sub> and SiN<sub>x</sub> in electronic device processing, and because of the chemical similarity of these surfaces. To explore ASD on SiN<sub>x</sub> and SiO<sub>2</sub>, we exposed blanket SiN<sub>x</sub> and SiO<sub>2</sub> wafers to multiple doses of molybdenum hexafluoride, MoF<sub>6</sub>, at low temperature (~200°C). Based on XPS analysis, the MoF<sub>6</sub> exposure leads to fluorination of both surfaces. Then, we performed polypyrrole (PPy) oxidative-CVD using pyrrole monomer and SbCl<sub>5</sub> as a surface oxidant. For the oxidative CVD process, 15 seconds of CVD produced ~50 nm of deposition on receptive surfaces. We found that PPy deposited readily on SiN<sub>x</sub> surface after some nucleation delay, but on SiO<sub>2</sub>, only isolated nuclei were formed. Control experiments using SiN<sub>x</sub> and SiO<sub>2</sub> substrates without the MoF<sub>6</sub> exposure step showed uniform deposition on both substrates. To extend this demonstration of ASD of SiN<sub>x</sub> vs SiO<sub>2</sub> to other materials and substrates, we tested ALD of TiO<sub>2</sub>, ZnO, and Al<sub>2</sub>O<sub>3</sub> SiO<sub>2</sub>, SiN<sub>x</sub> and Mo metal after exposure to MoF<sub>6</sub>. We find that this selective fluorination passivation of the SiO<sub>2</sub> surface allows for selective growth of TiO<sub>2</sub> and ZnO on Mo vs SiO<sub>2</sub>, whereas ALD Al<sub>2</sub>O<sub>3</sub> using TMA/H<sub>2</sub>O showed uniform, non-selective deposition. Moreover, after exposing SiO<sub>2</sub> and SiN<sub>x</sub> to MoF<sub>6</sub>, TiO<sub>2</sub> ALD using TiCl<sub>4</sub>/H<sub>2</sub>O deposited on SiN<sub>x</sub> after some delay, whereas a much longer delay was observed on SiO<sub>2</sub>. The mechanisms behind selectivity, and the extent of metal-fluoride exposure needed to achieve passivation is currently under investigation. Direct comparisons between metal oxide ALD nucleation on SiO<sub>2</sub>, SiN<sub>x</sub> and metal after exposure to MoF<sub>6</sub> will give insight into mechanisms necessary to achieve high selectivity, as well as provide options for advanced multi-material ASD schemes.

## Atomic Scale Processing Mini-Symposium

Room 116 - Session AP2+EM+PS+TF-MoA

### Modeling and Simulations of Atomic Layer Processing

Moderator: Satoshi Hamaguchi, Osaka University, Japan

#### 4:00pm AP2+EM+PS+TF-MoA-11 Atomistic Simulations on the Fundamental Aspects of Atomic Layer Processing (ALP), *Bonggeun Shong*, Hongik University, Republic of Korea **INVITED**

As size of electronic devices are miniaturized to nanoscale, the precision of their fabrication processes is becoming extremely demanding. Atomic layer deposition (ALD) is a vapor phase thin film deposition technique based on sequential, self-limiting surface reactions. Through ALD, high conformality on high-aspect ratio substrates, thickness control at the Angstrom level, and tunable film composition are achievable. Furthermore, area-selective ALD (AS-ALD) has recently emerged as a possible alternative bottom-up approach for nanoscale patterning. With these advantages, ALD is gaining interest as a powerful tool for many industrial and research applications, especially in microelectronic fabrication. Furthermore, atomic layer etching (ALE) is emerging as a novel technique that can provide atomically controlled etching of materials. These technologies with atomic layer precision are often altogether referred to as atomic layer processing (ALP). Ideally, the entire ALP processes are based only on the surface chemistry of the substrates. Thus, it is important to understand their surface reaction mechanisms in order to improve the process conditions and material quality, and even to design novel materials and processes. With development of modern simulation tools, utilization of atomistic calculations is becoming increasingly useful toward deeper understanding and design of such chemical reactions. However, ALD processes often face limitations toward fabrication of next-generation semiconductor devices due to their size scale and structural complexity; furthermore, such problems are often convoluted with challenges toward realistic simulations of surface chemical processes. In this talk, analysis of fundamental surface chemistry of various ALP based on computational chemistry methods, as well as development of new processes and materials based on chemical simulations will be presented.

#### 4:30pm AP2+EM+PS+TF-MoA-13 Understanding Process Parameters in High-Aspect-Ratio ALD via Transport Modeling, *Victor Vogt*, University of Michigan; *A. Gayle*, National Institute of Standards and Technology (NIST); *A. Miranda Manon*, *A. Lenert*, *N. Dasgupta*, University of Michigan

Atomic layer deposition (ALD) is a powerful tool to modify ultra-high-aspect-ratio structures with unparalleled conformality. We have recently demonstrated the ability of ALD to modify silica aerogels with aspect ratios greater than 60,000:1 and improve their thermal stability from ~600°C to ~800°C, for applications in concentrating solar thermal energy generation.<sup>1</sup> To facilitate conformal ALD modifications on these extreme aspect ratios, a reaction-diffusion model was developed to precisely predict infiltration into the aerogel as a function of exposure time and number of doses, enabling tunable control of the infiltration depth.<sup>2</sup>

In this study, we have built upon our previous reaction-diffusion model to explore the effects of exposure time, precursor temperature, and number of aerogels coated on process time and precursor utilization. We analyze process parameter trends in terms of the governing reaction-diffusion mechanism and relevant equations. These trends are then validated experimentally via energy dispersive x-ray spectroscopy (EDS) mapping of the infiltration depth. Additionally, we explore the relationship between number of aerogels coated and reactor volume, and we analyze the impacts of this on ALD reactor design for high-aspect-ratio substrates. Finally, we demonstrate that ALD can be used to tune the mechanical strength and stiffness of silica aerogels, a key limitation of these materials in practical applications. This work will enable a greater understanding of high-aspect-ratio ALD processing as well as its potential applications in the modification of porous materials.

References:

<sup>1</sup> Z.J. Berquist, A.J. Gayle, N.P. Dasgupta, and A. Lenert, Transparent Refractory Aerogels for Efficient Spectral Control in High-Temperature Solar Power Generation. *Adv. Funct. Mater.* **2022** *32*, 2108774.

<sup>2</sup> A.J. Gayle, Z.J. Berquist, Y. Chen, A.J. Hill, J.Y. Hoffman, A.R. Bielinski, A. Lenert, and N.P. Dasgupta, Tunable Atomic Layer Deposition into Ultra-High-Aspect-Ratio (>60000:1) Aerogel Monoliths Enabled by Transport Modeling, *Chem. Mater.* **2021** *33* (14), 5572-5583.

#### 4:45pm AP2+EM+PS+TF-MoA-14 Modeling Remote Inductively Coupled Plasmas for Plasma-Enhanced Atomic Layer Deposition, *Mackenzie Meyer*, *D. Boris*, *M. Johnson*, *J. Woodward*, *V. Wheeler*, US Naval Research Laboratory; *M. Kushner*, University of Michigan, Ann Arbor; *S. Walton*, US Naval Research Laboratory

Plasma-enhanced atomic layer deposition (PEALD) uses a plasma step to generate the necessary reactive species, allowing atomic layer deposition (ALD) processes to occur at lower temperatures and with additional reaction chemistries compared to thermal ALD. Remote inductively coupled plasma (ICP) sources are often used in PEALD as they limit electrons and ions at the growth substrate while providing radicals from the plasma. However, remote ICP systems, particularly downstream of the source, are not fully understood. Modeling of remote ICPs can contribute to an understanding of these systems. In this work, modeling of remote ICPs is performed using the 2D Hybrid Plasma Equipment Model (HPeM). The remote ICPs are based on the Veeco Fiji G1 and G2 sources operating in an N<sub>2</sub>/Ar mixture. Both inductively and capacitively coupled power contribute to the power deposited into the plasma. The results of the model are compared to experimental measurements reported, including atomic N density in the plasma source and electron density and plasma potential downstream in the spatial afterglow of the ICP. The model is also used to examine the production of species that are not measured, including metastable N<sub>2</sub>, as well as the absolute and relative fluxes of reactive species to the substrate, for a range of operating conditions. The results are then linked to the growth of nitride films in an effort to quantify the relative importance of different operating modes and reactive species. This work is partially supported by the Naval Research Laboratory base program.

#### 5:00pm AP2+EM+PS+TF-MoA-15 Prediction of Plasma-induced Changes in Surface Morphology and Composition during Atomic Layer Deposition: A Combined Ab-Initio and Monte Carlo Approach, *G. Hwang*, *Ting-Ya Wang*, University of Texas at Austin

Atomic layer deposition (ALD) has emerged as a method offering enhanced precision and control in comparison to traditional chemical vapor deposition. It operates through alternating cycles of two half-cycle reactions, ensuring sequential and self-limiting deposition. However, thermal ALD necessitates high deposition temperatures (> 400 °C), particularly for nitridation. Although employing plasma can reduce these surface temperatures, plasma can have detrimental effects on materials too, including modification of the chemical composition and densification, which profoundly impact crucial material properties such as dielectric constant.

Therefore, understanding the plasma-induced changes in surface morphology and composition is crucial. However, existing experimental techniques encounter limitations in surface analysis. Non-polar bonds, such as N<sub>2</sub> dimer, are inactive under infrared (IR) spectroscopy. X-ray photoelectron spectroscopy causes surface damage to a certain extent. Moreover, overlapping signals may render the analysis uncertain and challenging. Theoretical methods have their own set of limitations. Molecular dynamics (MD) simulations allow the study of dynamic processes but are constrained by limitations in both length and time scales, which make it unsuitable for ALD systems, where primary reactions fall into the category of rare events.

The integration of kinetic Monte Carlo (kMC) with density functional theory (DFT) presents a promising simulation approach for ALD. However, a notable challenge lies within kMC, specifically the requirement for a predefined list of permissible events. Traditionally, researchers identify a set of reactions considered most significant. Yet, given the numerous potential events occurring on a surface and the criticality of rare events in ALD, outcomes derived from a manually compiled list may sometimes lack authenticity.

We developed an atomistic, off-lattice, and three-dimensional simulator that integrates kMC and DFT, and employed a strategic approach to formulate a comprehensive event list, with the goal of encompassing a wide range of potential surface reactions. Our investigation centered on assessing the effects of N<sub>2</sub>, H<sub>2</sub>, and NH<sub>3</sub> plasmas on SiCN material, including examination of the roles played by radicals and ion bombardment. Furthermore, we also studied the influence of process conditions, including temperature and pressure, while also analyzing the influence of oxygen exposure.

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5:15pm **AP2+EM+PS+TF-MoA-16 Modelling and Simulation of Plasma-Enhanced Atomic Layer Deposition of Silicon Nitride Over Sidewall Surfaces of a Closing Narrow-Gap Trench**, *Jomar Tercero, K. Ikuse, S. Hamaguchi*, Osaka University, Japan

Molecular dynamics (MD) simulations were performed to study the transport mechanisms of chlorine (Cl) atoms during the plasma-enhanced atomic layer deposition (PE-ALD) of silicon nitride (SiN). PE-ALD is a technique to deposit highly precise and uniform thin films required for nanoscale semiconductor devices. The typical PE-ALD process involves sequential and self-limiting surface reactions, facilitating the formation of monolayers in a layer-by-layer manner.[1] In the case of SiN PE-ALD, chlorosilanes such as SiH<sub>2</sub>Cl<sub>2</sub> are commonly used as Si-containing gas precursors. During the first half-cycle, Si atoms of the precursors adsorb on the surface, whose surface atoms are then terminated by Cl atoms. Subsequently, the surface is exposed to nitrogen (N) and hydrogen (H)-containing plasmas. During this second half-cycle, H atoms react and capture Cl atoms on the surface, forming volatile hydrogen chloride (HCl) molecules.[2] In this study, our focus is PE-ALD of SiN over a trench structure when the gap is closing and the two facing sidewalls are approaching each other. In the desorption/nitridation half-cycle, Cl atoms must be removed from the extremely narrow gap by Cl or HCl diffusion if the gap is closing. The diffusion coefficients of Cl atoms in such narrow gaps were evaluated from molecular dynamics (MD) simulations, under different conditions for the surface temperature (700, 800, and 900 K), gap distance (0.6, 1, and 2 nm), and H density. The MD simulations revealed that, without H atoms, Cl diffusion was highly restricted. H atoms were observed to capture Cl atoms, assisting their transport in the narrow gap. Additionally, we observed the formation of H<sub>2</sub> molecules, some of which penetrated the SiN bulk and diffused. The results indicate that, as the two facing SiN sidewalls approach each other and the gap diminishes, the transport of atoms and molecules in the gap becomes restricted and therefore the ALE process slows down, eventually forming a seam between the two facing sidewalls.

## References

- [1] K. Arts, S. Hamaguchi, T. Ito, K. Karahashi, H. C. M. Knoop, A. J. M. Mackus, and W. M. M. E. Kessels, "Foundations of atomic-level plasma processing in nanoelectronics," *Plasma Sources Science and Technology*, 31, 103002 (2022).
- [2] R. A. Ovanessian, E. A. Filatova, S. D. Elliott, D. M. Hausmann, D. C. Smith, and S. Agarwal, "Atomic layer deposition of silicon-based dielectrics for semiconductor manufacturing: Current status and future outlook", *Journal of Vacuum Science and Technology A*, 37, 060904 (2019).

## Thin Films

### Room 115 - Session TF+AP-MoA

#### Thin Films Special Session: Remembering Dr. Paul Holloway II & Reception

**Moderators:** Sean Jones, Argonne National Laboratory, Philip Rack, University of Tennessee

1:30pm **TF+AP-MoA-1 A Surface Science Approach to Advancing Area-Selective Deposition and Atomic Layer Etching**, *Adrie Mackus*, Eindhoven University of Technology, Netherlands **INVITED**

With future nanoelectronics relying on the vertical stacking of devices, selective deposition and etching techniques are essential for enabling self-aligned processing of materials on such 3-dimensional devices structures. Similar to the research approach of dr. Paul. H. Holloway, in this work surface science methods are employed to obtain understanding of thin film processing. A combination of in-situ experiments and simulations is carried out to study the mechanisms of selectivity and inhibition.

Our work on area-selective atomic layer deposition (ALD) involves the use of small molecule inhibitors (SMIs) in three-step ALD cycles.<sup>1</sup> For example, diketone molecules can be used to inhibit the growth on various oxides surfaces. In-situ infrared spectroscopy studies previously revealed that the diketone acetylacetone (Hacac) can adsorb on an Al<sub>2</sub>O<sub>3</sub> surface in chelate and monodentate adsorption configurations.<sup>2</sup> Inspired on these insights, we recently developed atomic layer etching (ALE) processes based on etching by diketone dosing (e.g., hexafluoroacetylacetone) and plasma cleaning steps. Infrared spectroscopy and simulation studies suggest that the mechanism of etching with diketones involves a competition between etching and inhibition reactions. In this presentation, I will discuss how

inhibition reactions can be exploited for achieving either area-selective ALD or ALE, and highlight how surface science methods are crucial for understanding the underlying mechanisms.

1. Mackus *et al.*, *Chem. Mater.* **31**, 2 (2019)
2. Merx *et al.*, *Chem. Mater.* **32**, 3335 (2020)

2:00pm **TF+AP-MoA-3 Tuning Surface Radical Species for Area-Selective Initiated Chemical Vapor Deposition of Polymer Thin Films**, *Junjie Zhao*, Zhejiang University, China **INVITED**

Self-aligned bottom-up growth of polymer thin films is desired for non-lithographic patterning in applications ranging from nanostructure fabrication to device integration. Aiming at achieving area-selectivity for initiated chemical vapor deposition (iCVD), we developed a toolkit to tune the local concentration of radicals and thus the surface polymerization kinetics. We found that the radical concentration can be promoted locally by (1) generation on targeted surfaces, (2) trapping through gradient forces, and (3) retainment *via* reversible dormant species. *In-situ* quartz crystal microbalance was employed to investigate the reaction mechanisms involved in these area-selective iCVD processes. Cross-sectional imaging and spectroscopic microscopy confirmed the high selective of polymer deposition on the growth areas. Finally, we will show that these strategies are generally effective for area-selective deposition of poly(glycidyl methacrylate), poly(divinylbenzene) and cyclosiloxane polymers.

2:30pm **TF+AP-MoA-5 Recent Trends in Thermal ALD Chemistry**, *Markku Leskelä, G. Popov, M. Mattinen, A. Vihervaara, M. Ritala*, University of Helsinki, Finland

A review published in 2013 listed all the two-precursor ALD processes reported by the end of 2010 [1]. Since then, many new materials have been deposited by ALD and new processes have been developed for earlier known ALD materials. The recently published ALD database aims to provide a crowdsourced up-to-date collection of ALD processes [2]. In this presentation, we highlight the new precursor and thermal process chemistries published after 2010 based on the ALD database.

The data base contains 1725 unique thermal ALD processes for 548 thin film materials published between 1975 and 2023. The boom in ALD started around 1995 and the number of new processes reported annually increased from 20 in early 1990s to 60 in 2008. Since then, the number of new processes has remained at 60-80 each year. Since 2010, 991 new processes have been published for 441 materials from which 316 materials did not earlier have any ALD process.

Oxide processes form more than 50 % of all the published processes but their share has slightly decreased after 2010. Processes for chalcogenides, pnictides and elements are next in the list. Binary compounds clearly dominate the materials but after 2010 ternary and quaternary compounds as well as elements have increased their share. The number of new ternary processes is roughly double compared to new binary processes. From the ternary and quaternary compounds about 75 % are oxides. Before 2010 the five most common ligands used in metal precursors were halides, alkoxides, alkyls, β-diketonates and amides/imides. The order changes after 2010 to amides/imides, cyclopentadienyls, halides, alkoxides, and alkyls. Heteroleptic complexes have increased their share during the last decade. In non-metal precursors, reducing agents increased importance because of the increased interest to metal deposition.

New elements added to the ALD portfolio since 2010 are alkali metals (Na, K, Rb, Cs), Be, Re, Os, Au and Sb, the first five as oxides and latter four as elements. Reductive processes for transition metals are sought and first thermal processes have been reported for tin and chromium.

86 new binary materials were deposited by ALD since 2010 the biggest group being chalcogenides (29), halides (15) and oxides (15). These materials are linked to broader material and application trends, including perovskite solar (halides) and 2D materials (chalcogenides). Disulfide processes have been reported for Zr, Hf, Mo, Nb, Sn, Re and diselenides for Mo and W.

## References

- [1] V. Miikkulainen, M. Leskelä, M. Ritala, R.L. Puurunen, *J. Appl. Phys.* **113**, (2013) 021301.
- [2] <https://www.atomiclimits.com/alddbatabase/>

2:45pm **TF+AP-MoA-6 Ultrathin Polymers Films: Smart Materials and Functionality**, *Rigoberto Advincula*, University of Tennessee Knoxville  
Nanostructuring involves the application of materials and processing methods to achieve unique dimensional structures at the nanoscale. Soft matter looks at polymers and the self-assembly and directed assembly of

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macromolecules that results in a unique function, e.g. sensors, electronic actuators, microfluidics, etc.. The research and development of smart or intelligent surfaces and coatings capable of stimuli-response or Omni behavior represent an essential development for coatings in any major application. The ability to control wetting through nanostructuring and choice of chemical functionality can be supplemented by the right deposition methods or application of both lithographic and non-lithographic printing methods. In particular, we have used: 1) polymer grafting, 2) polyelectrolyte layer-by-layer deposition, 3) molecular imprinting of polymers, 4) electro-nanopatterning method using conducting AFM and 5) colloidally templated arrays. Until now, colloidal template 2D electropolymerization remains largely an unexplored method, and there are only a few accounts on colloidal template electropolymerization techniques for micropatterning polymer films. But combined with electropolymerization and polymer brushes it is possible to have functional polymer films that can have sensing and controlled wettability. We will be reporting on the use of stereolithographic lithography (SLA) to create functional superhydrophobic surfaces and nanoreactors.

3:00pm **TF+AP-MoA-7 Growing Polymers Molecule by Molecule Through Vapor Deposition**, *Matthias J. Young*, University of Missouri-Columbia; *N. Paranamana, M. Mehregan, S. Mehregan, A. Datta*, University of Missouri, Columbia **INVITED**

Controlling the sequence of monomers within a copolymer is challenging. Solid-phase peptide synthesis provides molecular sequence control of amino acids by employing solution-phase synthesis with removable protecting groups. This technique was awarded a Nobel prize in 1984 and has spawned a revolution in molecular biology and biochemistry over the last fifty years. However, this approach for peptide synthesis is not readily transferrable to other classes of polymers. Here, we summarize our efforts over the last five years to provide molecular sequence control in polymers formed by oxidative polymerization by employing self-limiting vapor-phase surface reactions through a process termed oxidative molecular layer deposition, or oMLD. We describe insights into the mechanism of oMLD growth that facilitates molecular sequence control, and we examine how molecular sequence impacts redox activity and electronic conductivity. We discuss the various oMLD homopolymer and copolymer chemistries that have been developed to date, expanding from the first oMLD homopolymer chemistry in 2014 to seven oMLD homopolymer chemistries in 2024, and the outlook for oMLD growth of hundreds of potential homopolymer chemistries and a factorial number of copolymer chemistries. We demonstrate the ability to form ultrathin conformal polymer coatings by oMLD and we discuss the application of these thin film coatings to electrochemical energy storage and ion sensors. We also discuss opportunities for improving on current oMLD synthesis techniques and how the knowledge we have gained about oMLD growth may inform the development of other layer-by-layer vapor-phase polymerization chemistries.

3:30pm **TF+AP-MoA-9 Solar Cells, Sensors, and Sensorimotor Neural Prosthetics: My Branch of the Holloway Tree**, *Loren Rieth*, West Virginia University **INVITED**

Professor Paul Holloway was my PhD mentor from 1994 to 2001. "Doc's" combination of down-to-earth practicality, erudite knowledge of fundamental materials science, absence of hubris, and mischievous sense of humor resonated with me then and now. His passion for science and engineering was clear from the hours he kept (his modest car was always one of the first to arrive in the morning), his joy when learning something new, and the sustained research productivity he achieved. He balanced this with helping Bette run the family farm, hunting gators, and a love for the Florida outdoors. It was an honor, privilege, and joy to have him as a mentor. The exemplary training I received in the Holloway group on thin film semiconducting materials for solar cell included vicarious learning about luminescent and optical materials and Ohmic semiconductor contacts. This led to my research in metal oxide gas sensors, harsh environment MEMS, and ultimately neural interface microelectrode research and development, the focus of my technical talk.

My neural interface research focuses on penetrating neural electrodes based on micromachined silicon, and flexible neural interfaces based on polyimide microfabrication. Rapid progress is being made in technologies to record, stimulate, and modulate the nervous system. These advancements are being made both to treat diseases with new medical device technologies, and also as tools for basic neuroscience research. Treatments enabled by neural interfaces include controlling bionic limbs for patients with amputations or paralysis, restoring senses (hearing, vision, and touch),

treating inflammatory diseases, controlling metabolic diseases, helping to restore mental health, and many others. Currently, successful devices such as cochlear implants, deep brain stimulators, and vagus nerve stimulators, rely on macro-electrodes fabricated using bulk materials. This limits their ability to scale towards interfacing the billions of neurons that comprise the nervous system. Materials science plays a critical role in the development of penetrating and flexible micro-electrode technologies. I'll highlight development and use of Utah Slanted Electrode Arrays in the peripheral and central nervous system, and their associated materials challenges. Additionally, recent developments regarding advanced polyimide-based flexible electrodes and optical neural interfaces for small (e.g. 100  $\mu\text{m}$  diameter) peripheral nerves will be presented. An important example is the vagus nerve of murine models, which can be modulated to regulate the autonomic nervous system, a technique called bioelectronic medicine.

## 2D Materials

Room 122 - Session 2D+AP+EM+QS+SS+TF-TuM

### 2D Materials: Synthesis and Processing

Moderators: **Jyoti Katoch**, Carnegie Mellon University, **Huamin Li**, University at Buffalo-SUNY

8:00am **2D+AP+EM+QS+SS+TF-TuM-1 Tailored Growth of Transition Metal Dichalcogenides Monolayers and Their Heterostructures, *Andrey Turchanin***, Friedrich Schiller University Jena, Germany **INVITED**

Two-dimensional materials (2D), their van der Waals and lateral heterostructures possess a manifold of unique electronic, optoelectronic and photonic properties which make them highly interesting for fundamental studies and technological applications. To realize this potential, their tailored growth as well as understanding of the role of their intrinsic defects and 2D-material/substrate interactions are decisive. In this talk, I will present an overview of our recent progress on the synthesis by chemical vapor deposition (CVD), material characterization and studying of fundamental electronic and photonic properties of 2D transition metal dichalcogenide (TMDs) including some applications in electronic and optoelectronic device as well as observing of new excitonic phenomena. A particular focus will be on the lateral heterostructures of TMD monolayers with atomically sharp boundaries and Janus TMDs.

#### References

- [1] A. George et al. *J. Phys. Mater.* **2**, 016001, 2019.
- [2] S. Shree et al. *2D Mater.* **7**, 015011, 2020.
- [3] I. Paradeisanos et al. *Nat. Commun.* **11**, 2391 (2020).
- [4] G. Q. Ngo et al., *Adv. Mater.* **32**, 2003826 (2020).
- [5] A. George et al. *npj 2D Mater. Appl.* **5**, 15 (2021).
- [6] S. B. Kalkan et al., *npj 2D Mater. Appl.* **5**, 92 (2021).
- [7] E. Najafidehaghani et al. *Adv. Funct. Mater.* **31**, 2101086 (2021).
- [8] Z. Gan et al. *Adv. Mater.* **34**, 2205226 (2022).
- [9] Z. Gan et al. *Small Methods* **6**, 2200300 (2022).
- [10] D. Beret et al., *npj 2D Mater. Appl.* **6**, 84 (2022).
- [11] G. Q. Ngo et al. *Nat. Photonics* **16** 769-776 (2022)
- [12] S.B. Kalkan, *Adv. Opt. Mater.* **11**, 2201653 (2023).
- [13] R. Rosati et al., *Nat. Commun.* **14**, 2438 (2023).
- [14] H. Lamsaadi et al., *Nat. Commun.* **14**, 5881 (2023).
- [15] J. Picker et al., *Nanoscale Adv.* **6**, 92-101 (2024).

8:30am **2D+AP+EM+QS+SS+TF-TuM-3 High-Coverage MoS<sub>2</sub> Growth by Two-Step Annealing Process, *Shinichi Tanabe*, H. Miura**, Tokyo Electron Ltd., Japan; *N. Okada*, *T. Irisawa*, AIST, Japan; *Y. Huang*, *H. Warashina*, *A. Fukazawa*, *H. Maehara*, Tokyo Electron Ltd., Japan

Continuation of Moore's Law scaling requires thin channels in nanosheet field-effect transistor architecture. In this respect, transition-metal dichalcogenides (TMDs) are candidates for the channel material because TMDs are expected to show higher mobility than Si when thickness of the channel is extremely thin. Compatibility to Si nanosheet field-effect transistor fabrication process requires TMD/buffer multilayer film. To obtain such film, alternative preparation of TMD and buffer layers is necessary. Although high-quality TMD can be obtained on a buffer layer by transferring TMD from other substrates, development of a reliable transferring method is challenging. Thus, direct growth of a TMD on a buffer layer is preferable.

We report on a successful growth of high-coverage MoS<sub>2</sub> on SiO<sub>2</sub>/Si substrate. The process starts with growing an initial film on SiO<sub>2</sub>/Si substrate. Here, a continuous initial film can be easily grown by this process with high growth rate. Next, the initial film is sulfurized by a first annealing step followed by crystallization of the film by a second annealing step. The obtained film is a continuous layered film which was confirmed by cross-sectional TEM images. In addition, typical Raman spectra consisted of E<sub>2g</sub> and A<sub>1g</sub> peaks are observed in entire substrate which shows that MoS<sub>2</sub> is grown with high coverage. The difference of E<sub>2g</sub> and A<sub>1g</sub> peaks is about 21 cm<sup>-1</sup>. These results indicate that the two-step annealing process is suitable for obtaining MoS<sub>2</sub> in large area.

8:45am **2D+AP+EM+QS+SS+TF-TuM-4 Anomalous Isotope Effect on the Optical Bandgap in a Monolayer Transition Metal Dichalcogenide Semiconductor, *Kai Xiao***, Center for Nanophase and Materials Sciences Oak Ridge National Laboratory; *Y. Yu*, School of Physics and Technology, Wuhan University, China; *V. Turkowski*, Department of Physics, University of Central Florida; *J. Hachtel*, Center for nanophase and Materials Sciences Oak Ridge National Laboratory; *A. Puzetzyk*, *A. Ievlev*, *C. Rouleau*, *D. Geohegan*, Center for Nanophase and Materials Sciences Oak Ridge National Laboratory

Isotope effects on optical properties of atomically thin 2D materials have rarely been studied to date due to significant challenges posed by sample-to-sample variations resulting from defects, strain, and substrate interactions, complicating the interpretation of optical spectroscopic results. Here, we report a novel two-step chemical vapor deposition method to synthesize isotopic lateral junctions of MoS<sub>2</sub>, comprising monolayer single crystals with distinct isotopic regions. This method allowed the minimization of shifts in photoluminescence due to synthetic heterogeneities necessary to confirm the intrinsic isotope effect on the optical band gap of 2D materials. Raman measurements and temperature-dependent photoluminescence spectra revealed an unusual 13 (± 7) meV redshift as the Mo isotope mass increased in monolayer MoS<sub>2</sub>. This shift is distinct from the trend observed in conventional semiconductors and quantum wells (Si, GaAs, diamond, hBN, etc.). Our experimental characterization, along with time-dependent density-functional theory (TDDFT) and many-body second-order perturbation theory, disclosed that this anomalous shift in the optical band gap in 2D MoS<sub>2</sub> resulted from significant changes in the exciton binding energy induced by strong exciton-phonon scattering. This study provides fundamental insights into understanding the effect of exciton-phonon scattering on the optoelectronic properties of atomically thin 2D materials.

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

9:00am **2D+AP+EM+QS+SS+TF-TuM-5 CVD Growth and Characterization of High-Quality Janus SeMoS and SeWS Monolayers, *Julian Picker***, Friedrich Schiller University Jena, Germany; *M. Ghorbani-Asl*, Helmholtz Zentrum Dresden-Rossendorf, Germany; *M. Schaal*, *O. Meißner*, *F. Otto*, *M. Gruenewald*, *C. Neumann*, *A. George*, Friedrich Schiller University Jena, Germany; *S. Kretschmer*, Helmholtz Zentrum Dresden-Rossendorf, Germany; *T. Fritz*, Friedrich Schiller University Jena, Germany; *A. Krashennnikov*, Helmholtz Zentrum Dresden-Rossendorf, Germany; *A. Turchanin*, Friedrich Schiller University Jena, Germany

Structural symmetry breaking of two dimensional (2D) materials leads to novel physical phenomena. For 2D transition metal dichalcogenides (TMDs) such symmetry breaking can be achieved by exchange of one chalcogen layer with another one. The resulting, so-called Janus TMD structure exhibits an intrinsic dipole moment due to the different electronegativity values of the top and bottom chalcogen layers. Since Janus TMDs do not exist as bulk crystals, they cannot be obtained by exfoliation and need to be synthesized. Recently, we developed a route to grow Janus SeMoS monolayers (MLs) by chemical vapor deposition (CVD). [1] In this approach MoSe<sub>2</sub> monolayers are firstly grown on Au foils and then sulfurized to exchange the bottom selenium layer with sulfur atoms. The formation of high-quality Janus SeMoS MLs and the growth mechanism are proven by Raman and X-ray photoelectron spectroscopy (XPS), photoluminescence measurements, transmission electron microscopy and density functional theory (DFT). Here we present an investigation down to the atomic scale of Janus SeMoS MLs grown on Au(111). From low-energy electron diffraction (LEED) and scanning tunneling microscopy (STM) measurements we determine experimentally the lattice parameters of Janus SeMoS for the first time. The obtained results are in good agreement with the respective DFT calculation. Based on the angle-resolved ultraviolet photoelectron spectroscopy (ARUPS) study, we also obtain the spin-orbit splitting value of the valence band at the K point. Moreover, applying the same approach, we grow and characterize Janus SeWS MLs and provide a comparative analysis with the Janus SeMoS system.

- [1] Z. Gan, I. Paradeisanos, A. Estrada-Real, J. Picker, C. Neumann, A. Turchanin et al., *Chemical Vapor Deposition of High-Optical-Quality Large-Area Monolayer Janus Transition Metal Dichalcogenides*, *Adv. Mater.* **34**, 2205226 (2022).

# Tuesday Morning, November 5, 2024

9:15am **2D+AP+EM+QS+SS+TF-TuM-6 Location-Selective CVD Synthesis of Circular MoS<sub>2</sub> Flakes with Ultrahigh Field-Effect Mobility**, *Chu-Te Chen, A. Cabanillas, A. Ahmed, A. Butler, Y. Fu, H. Hui, A. Chakravarty, H. Zeng*, University at Buffalo-SUNY; *A. Yadav*, Applied Materials, Inc.; *H. Li*, University at Buffalo-SUNY; *K. Wong*, Applied Materials, Inc.; *F. Yao*, University at Buffalo-SUNY

Two-dimensional (2D) semiconducting transition metal dichalcogenides (TMDs) have been considered as promising channel material candidates for future nanoelectronics. The device performance has been significantly improved over the years due to the advancements in understanding of TMD materials, device design, and fabrication process. Despite the early success in demonstrating proof-of-concept devices, scalable and single-crystal growth of TMD films on suitable substrates remains a formidable roadblock to the development of commercially viable TMD-based nanoelectronics. To mitigate this problem, we exploit a controlled growth of high-quality TMD layers at desired locations and demonstrate excellent and consistent electronic properties in transistor device architectures. Taking MoS<sub>2</sub> as an example, we develop a precursor-seeded growth strategy for the direct and site-specific synthesis on SiO<sub>2</sub> substrates using chemical vapor deposition (CVD). By employing electron-beam lithography to pattern seed layers, precise nucleation and growth at designated positions are achieved. Through systematic exploration of CVD synthesis parameters, ordered arrays of circular MoS<sub>2</sub> flakes are successfully grown with the MoO<sub>3</sub> seeds serving as the nucleation sites. A comprehensive suite of microscopic/spectroscopic characterizations along with electrical measurements is utilized to analyze the microstructural and transport properties of the as-grown MoS<sub>2</sub> flakes. The tri-layer circular MoS<sub>2</sub> arrays possess an adjustable and uniform size and exhibit a consistent field-effect mobility up to ~20 cm<sup>2</sup>/V·s with Bi/Au electrode contacts. These findings showcase a technological breakthrough to 2D material synthesis and hold great promise for future integration of 2D materials in the next generation nanoelectronics.

9:30am **2D+AP+EM+QS+SS+TF-TuM-7 Optoelectronic Properties of Exfoliated and CVD Grown TMD Heterostructures**, *Elycia Wright, K. Johnson, S. Coye, M. Senevirathna, M. Williams*, Clark Atlanta University

Transition metal dichalcogenides (TMDs) have attracted significant attention due to their distinctive electronic band structures, which result in intriguing optoelectronic and magnetic properties such as direct bandgap in the visible-infrared range, large exciton binding energies and the presence of two intrinsic valley-contrasting quantities—the Berry curvature and the orbital magnetic moment. Researchers have recently shown interest in studying heterostructures made from different TMD materials. The idea is to combine these materials to create synergistic effects, which can result in even more exciting properties than those found in individual TMDs. For instance, MoS<sub>2</sub>/WS<sub>2</sub> heterostructure can exhibit novel and enhanced optoelectronic performances, including bipolar doping and photovoltaic properties. TMD-based heterostructures may open many possibilities for discovering new physics and developing novel applications. While the science of TMDs and TMD-based heterostructures has made significant strides over the past decade, the field has not yet matured. Numerous challenges, particularly in realizing TMD-based practical applications, remain unresolved. This underscores the importance of our collective efforts in pushing the boundaries of this field.

Exfoliation is a common method for assembling TMD heterostructures, but it has limitations in producing TMD heterostructures on a large scale. The chemical vapor deposition (CVD) method can be used to grow TMD heterostructures on a large scale, which is required in massive device production. However, there are numerous challenges in growing high-quality TMD heterostructures with large areas by CVD, which need to be solved before TMD-based practical applications can be achieved. Our research will focus on the growth of heterostructures (MoS<sub>2</sub>/WS<sub>2</sub>) on various substrates (such as sapphire and SiO<sub>2</sub>/Si) using chemical vapor deposition (CVD). We will explore different mechanisms to achieve large area heterostructures and compare the resulting optoelectronic properties with exfoliated heterostructures. The properties will be characterized using Raman and Fourier Transform infra-red (FTIR) spectroscopy and confocal laser optical microscopy.

9:45am **2D+AP+EM+QS+SS+TF-TuM-8 Pulsed Laser Deposited Amorphous Boron Nitride for 2D Materials Encapsulation**, *Daniel T. Yimam, S. Harris, A. Puzetky, I. Vlasiouk, G. Eres, K. Xiao, D. Geohegan*, Oak Ridge National Laboratory, USA

Recent advancements in 2D materials have opened new avenues in optoelectronics and microelectronics. However, their integration is

hindered by challenges related to materials stability and degradation. Realizing the full potential of 2D materials requires synthesizing and functionalizing an encapsulation layer with desired properties. Recently amorphous boron nitride (aBN) has attracted attention as an ideal low-k material suitable for 2D electronics due to its effectiveness as a protective encapsulation layer. Unlike hexagonal boron nitride (h-BN), which requires high temperatures for deposition and poses challenges for large-area synthesis and integration, aBN can be deposited at significantly lower temperatures. This property makes aBN highly attractive and compatible for back-end-of-line (BEOL) processes in the semiconductor industry.

In this work, we demonstrate that pulsed laser deposition (PLD) enables the deposition of aBN with precise kinetic energy control of precursors, facilitating direct deposition onto 2D materials without significant defect formation. Various in situ plume diagnostics and monitoring tools during deposition were utilized to identify optimal deposition conditions, ensuring ideal kinetic energy ranges and accurate thickness control. This enhances the aBN as an effective encapsulation and barrier against 2D materials thermal degradation, while improving photoluminescence of encapsulated 2D materials. We believe our work significantly impacts future microelectronics by providing low thermal budget method for encapsulating 2D materials and understanding strain and defect evolution. Our work not only advances the practical applications of 2D materials but also paves the way for in situ experimental analysis and diagnostics in the field of material science.

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

**Keywords:** Pulsed Laser Deposition, Amorphous Boron Nitride, 2D Materials, Encapsulation, In Situ Diagnostics.

11:00am **2D+AP+EM+QS+SS+TF-TuM-13 Topotaxy for Compositional Variations of Transition Metal Dichalcogenides**, *Matthias Batzill*, University of South Florida

Topotaxy is a kind of solid-state reaction in which the product crystal is crystallographically related to the initial crystal. In 2D materials the initial crystal could be a single sheet or a few layers that are being reacted with same or dissimilar elements to produce novel 2D materials that may not exist in the bulk. Here we investigate such topotactical reactions for transition metal dichalcogenides (TMDs) by reacting them with vapor deposited transition metals. This can result in phase transformations of known layered materials, such as PtTe<sub>2</sub> + Pt => Pt<sub>2</sub>Te<sub>2</sub> [1], new phases such as mirror twin grain boundary networks in MoSe<sub>2</sub> or MoTe<sub>2</sub> [2], or covalently linking bi-layer TMDs by intercalants of the same or different TMs [3]. The studies are performed on MBE grown TMDs and are further modified by post-growth reaction with TM. The resulting structures are characterized by surface probes, such as STM, photoemission, and LEED. In general, the open structure of many 2D materials make them ideal for topotaxy and provide an approach for modifying their composition and induce new properties. Moreover, it allows to locally modify an extended 2D sheet and thus produce in-plane heterojunctions between ‘original’ and modified 2D domains in a first step to create in-plane device structures.

[1] P.M. Coelho, H.P. Komsa, H. Coy Diaz, Y. Ma, A.V. Krasheninnikov, M. Batzill.

Post-Synthesis Modifications of Two-Dimensional MoSe<sub>2</sub> or MoTe<sub>2</sub> by Incorporation of Excess Metal Atoms into the Crystal Structure.

ACS Nano 12, 3975-3984 (2018)

[2] K. Lasek, J. Li, M. Ghorbani-Asl, S. Khatun, O. Alanwoko, V. Pathirage, A.V. Krasheninnikov, M. Batzill.

Formation of In-Plane Semiconductor–Metal Contacts in 2D Platinum Telluride by Converting PtTe<sub>2</sub> to Pt<sub>2</sub>Te<sub>2</sub>.

Nano Letters 22, 9571-9577 (2022)

[3] V. Pathirage, S. Khatun, S. Lisenkov, K. Lasek, J. Li, S. Kolekar, M. Valvidares, P. Gargiani, Y. Xin, I. Ponomareva, M. Batzill.

2D Materials by Design: Intercalation of Cr or Mn between two VSe<sub>2</sub> van der Waals Layers.

Nano Letters 23, 9579-9586 (2023)

11:15am **2D+AP+EM+QS+SS+TF-TuM-14 Solid State Reaction Epitaxy to Create van der Waals Heterostructures between Topological Insulators and Transition Metal Chalcogenides**, *Salma Khatun, O. Alanwoko, V. Pathirage, M. Batzill*, University of South Florida

Van der Waals (vdW) heterostructures have emerged as a promising avenue for exploring various quantum phenomena. However, the formation of these heterostructures directly is complicated, as individual materials could have different growth temperatures, and alloying can occur at the interface. We present an alternative process akin to a solid-state reaction to modify the surface layer of quantum materials and introduce new properties. Specifically, we used vapor-deposited transition metals (TMs), Cr and Mn, with the goal to react with  $\text{Bi}_2\text{Se}_3$  and transform the surface layer into  $\text{XBi}_2\text{Se}_4$  ( $X = \text{Cr, Mn}$ ). Our results demonstrate that the TMs have a high selenium affinity that drives Se diffusion toward the TM. We found that when a monolayer of Cr is evaporated, the surface  $\text{Bi}_2\text{Se}_3$  is reduced to  $\text{Bi}_2$ -layer, and a stable (pseudo) 2D  $\text{Cr}_{1+x}\text{Se}_2$  layer is formed, whereas  $\text{MnBi}_2\text{Se}_4$  phase is formed with a mild annealing for monolayer amount of Mn deposition.<sup>[1]</sup> However, this phase only occurs for a precise amount of initial Mn deposition. Sub-monolayer amounts dissolve into the bulk, and multilayers form stable MnSe adlayers. Our study highlights the delicate energy balance between adlayers and desired surface-modified layers that govern the interface reactions.<sup>[1]</sup> The success of obtaining the  $\text{MnBi}_2\text{Se}_4$  septuple layer manifests a promising approach for engineering other multicomponent vdW materials by surface reactions.

## REFERENCE

[1] S. Khatun, O. Alanwoko, V. Pathirage, C. C. de Oliveira, R. M. Tromer, P. A. S. Autreto, D. S. Galvao, and M. Batzill, *Adv. Funct. Mater.* **2024**, 2315112

11:30am **2D+AP+EM+QS+SS+TF-TuM-15 AVS National Student Awardee Talk: Quasi-Van Der Waals Epitaxial Growth of Thin  $\gamma'$ -GaSe Films**, *Mingyu Yu*<sup>1</sup>, University of Delaware; *S. Law*, Pennsylvania State University

As an advanced two-dimensional (2D) layered semiconductor, GaSe has various appealing properties, such as rare intrinsic p-type conductivity, nonlinear optical behavior, high transparency in 650-1800nm, and a shift from an indirect-bandgap single-layer film to a direct-bandgap bulk material. These features make GaSe rich in potential in quantum photonic devices, field-effect transistors, photodetectors, etc. GaSe has a hexagonal crystal structure composed of Se-Ga-Ga-Se quadruple layers (QLs). Each QL is bonded by weak van der Waals (vdW) forces, enabling multiple polymorphs:  $\epsilon$ -(2H),  $\beta$ -(2R),  $\delta$ -(4H), and  $\gamma$ -(3R). They have identical non-centrosymmetric QL with a  $D_{3h}$  space group. Besides the four extensively explored polymorphs, a new polymorph,  $\gamma'$ -(3-R) GaSe, was proposed for the first time in 2018.  $\gamma'$ -GaSe is unique for its centrosymmetric  $D_{3d}$  QL (Fig. S1), for which  $\gamma'$ -GaSe is predicted to show intriguing properties compared to other polymorphs. However, there are few existing reports on the observation of  $\gamma'$ -GaSe due to its less-favorable formation energy. Moreover, the wafer-scale production of pure GaSe single crystal thin films remains challenging because of the coexistence of stable multiphases and polymorphs.

We developed a quasi-vdW epitaxial growth method to obtain high-quality pure  $\gamma'$ -GaSe nanometer-thick films on GaAs(111)B at a wafer scale. It results in GaSe thin films exhibiting a smooth surface with a root-mean-square roughness as low as 7.2 Å (Fig. S2a) and a strong epitaxial relationship with the substrate (Fig. S2b). More interestingly, we observed a pure  $\gamma'$ -polymorph using scanning transmission electron microscopy (Fig. S2c,d). Through density-functional theory analysis (Fig. S3),  $\gamma'$ -GaSe can be stabilized by Ga vacancies since its formation enthalpy tends to become lower than that of other polymorphs when Ga vacancies increase. We also observed that, unlike other GaSe polymorphs,  $\gamma'$ -GaSe is inactive in room-temperature photoluminescence tests. This may be related to its centrosymmetric QL structure, which we are exploring further. Meanwhile, we systematically studied the growth window for GaSe with high structural quality and identified that GaAs(111)B is more suitable than c-sapphire as a substrate for GaSe growth. Overall, this study advances the wafer-scale production of  $\gamma'$ -GaSe films, and elucidates a method for direct epitaxial growth of hybrid 2D/3D heterostructures with atomically sharp interfaces, facilitating the development of heterogeneous integration. In the future, we will focus on developing the properties and applications of  $\gamma'$ -GaSe, and delving into the understanding of the epitaxial growth mechanism.

11:45am **2D+AP+EM+QS+SS+TF-TuM-16 Investigation of Dry Transfer of Epitaxial Graphene from SiC(0001)**, *Jenifer Hajjuz, D. Pennachio, S. Mack, R. Myers-Ward*, U.S. Naval Research Laboratory

Transfer of high-quality graphene from its growth substrate to substrates of technological interest can be necessary to enable its use in certain applications, however it remains challenging to achieve large-area transfer of graphene that is clean and intact. This work utilizes a dry transfer technique in which an adhesive metal stressor film is used to exfoliate epitaxial graphene (EG) from SiC(0001) [1]. In this method, the strain energy in the metal film must be high enough to allow for uniform exfoliation, but low enough such that self-exfoliation of graphene does not occur.

We investigate the dry transfer of monolayer EG (MEG) and hydrogen-intercalated, quasi-freestanding bilayer graphene (QFBEG) grown by sublimation of Si from nominally on-axis 6H-SiC(0001) in a CVD reactor in Ar ambient. A magnetron sputtered Ni stressor layer is used to exfoliate EG and transfer to GaAs, glass, and  $\text{SiO}_2/\text{Si}$  substrates. The Ar pressure during sputtering is found to impact the stress, film density, and roughness of the Ni film, as determined from wafer curvature and X-ray reflectivity (XRR) measurements. By using appropriate sputtering conditions, the Ni/graphene film exfoliates from the entire area of the SiC substrate with use of thermal release tape. Atomic force microscopy (AFM), scanning electron microscopy, Raman spectroscopy, x-ray photoelectron spectroscopy (XPS), and Nomarski microscopy are used to characterize the graphene. The Ni 2p peak was not detected in XPS of the transferred graphene after removal of the Ni film by etching in acid. Additionally, XPS revealed minimal oxide present at the graphene-GaAs interface, consistent with previous reports for this dry transfer method [2].

Raman spectroscopy mapping showed that predominately monolayer graphene is transferred from MEG, while predominately bilayer graphene is transferred from QFBEG. Raman spectroscopy of the SiC substrate after MEG exfoliation shows the  $6\sqrt{3}$  buffer layer that forms during growth on SiC(0001) remains on the SiC substrate. Consequently, if there are regions of exposed  $6\sqrt{3}$  buffer layer in the as-grown MEG on SiC, AFM shows that there are corresponding gaps in the transferred graphene film where the areas of exposed buffer layer do not transfer. The  $6\sqrt{3}$  buffer layer is not present in QFBEG due to the hydrogen-intercalation process. It is found that the same Ni sputtering conditions that led to uniform exfoliation and transfer of MEG result in micron-scale tears in the Ni/QFBEG film. By lowering the strain energy in the sputtered Ni film, these tears can be reduced or eliminated.

[1] Kim, J., *et al.*, *Science*, 342, 833 (2013).

[2] Kim, H., *et al.*, *ACS Nano*, 15, 10587 (2021).

12:00pm **2D+AP+EM+QS+SS+TF-TuM-17 Nickel Foams Enable Space-Confined Chemical Vapor Deposition (CVD) Synthesis of High-Quality MoS<sub>2</sub> Films**, *Taylor Currie, L. Tetard, T. Jurca*, University of Central Florida

Space-confined chemical vapor deposition (CVD) is a variation on traditional CVD syntheses in which the space between the substrate and precursor is restricted, which can lead to more consistent growth of high-quality two-dimensional (2D) materials. Space-confinement can be achieved by, for example, (1) using a shorter tube of smaller diameter inside the reactor tube, or (2) placing the substrate and precursor very close to each other. In both cases the concentration of reactants reaching the substrate is limited, which prevents excessive and rapid (lateral) growth and instead favors 2D film growth. In our approach, a growth substrate (c-plane sapphire wafer) was placed directly on top of nickel foam (NF) pre-loaded with molybdenum oxide ( $\text{MoO}_x/\text{NF}$ ). A quartz boat containing sulfur powder was placed upstream in a 275 °C temperature zone, and a second boat containing the substrate and  $\text{MoO}_x/\text{NF}$  was placed in a separately controlled temperature zone at 850, 900, or 950 °C. Using this approach, high-quality  $\text{MoS}_2$  monolayers were grown at 1, 5, or 15 min, as confirmed by optical microscopy, Raman and photoluminescence spectroscopies, energy-dispersive x-ray spectroscopy, and atomic force microscopy. We determined that the quality and thickness (i.e. monolayer, few layer, multilayer, bulk) of the  $\text{MoS}_2$  films were dependent on temperature and hold time used for the growth, with trials at 850 °C for 15 min, 900 °C for 15 min, and 950 °C for 5 min resulting in the best films. The use of a readily available metal foam with inherent porosity enhances the ease and accessibility of this space-confined CVD approach. This provides many more opportunities for modifications (e.g. varying the metal precursor used to decorate NF, surface coverage of precursor on NF, porosity of NF, and/or distance between substrate and NF).

<sup>1</sup> AVS National Student Awardee

## Atomic Scale Processing Mini-Symposium

### Room 116 - Session AP1+EM+PS+TF-TuM

#### Atomic Layer Etching I: Thermal Processes

Moderators: Steven M. George, University of Colorado at Boulder, Austin Minnich, California Institute of Technology

8:00am **AP1+EM+PS+TF-TuM-1 Highly Selective and Isotropic Atomic Layer Etching using Dry Chemical Removal**, Nobuya Miyoshi, Hitachi High-Tech America, Inc. **INVITED**

As semiconductor devices shrink to sub-10 nm dimensions, the introduction of new device structures, integration schemes, and materials brings many challenges to device manufacturing processes. A new structure with gate-all-around (GAA) nanosheets has been introduced to reduce the power consumption of transistors and achieve higher transistor integration density. For advanced semiconductor memory devices, 3D NAND flash has been introduced to achieve higher bit densities. Fabricating these three-dimensional (3D) devices requires isotropic etching of thin films with atomic layer control, high selectivity to underlying materials, and high uniformity over high-aspect-ratio 3D structures. Thermal atomic layer etching (ALE) is a promising method for isotropic etching with atomic-level precision and high conformality over three-dimensional structures. We developed a dry chemical removal (DCR) tool with an infrared (IR) wafer annealing and quick cooling system to perform highly selective thermal ALE for various materials. Thermal ALE was demonstrated for  $\text{Si}_3\text{N}_4$  and  $\text{SiO}_2$  films using the formation and desorption of  $(\text{NH}_4)_2\text{SiF}_6$ -based surface-modified layers. Thermal ALE processes for W and TiN films were also demonstrated by the formation and desorption of halogenated surface-modified layers. These ALE processes show a self-limiting formation of modified layers, enabling conformal and precisely controlled etching. In addition, spontaneous and highly selective etching of  $\text{SiO}_2$  was demonstrated on the DCR tools using  $\text{HF}/\text{CH}_3\text{OH}$  vapor.  $\text{SiO}_2$  films can be etched spontaneously with high selectivity to SiN films when the temperature of the substrate is lower than  $-20^\circ\text{C}$ .

8:30am **AP1+EM+PS+TF-TuM-3 Selective Si or Ge Dry, Thermal Spontaneous Etching Using HF Vapor**, Marcel Junige, T. Collieran, S. George, University of Colorado Boulder

Advanced 3D structures in microelectronics require novel self-aligned techniques. For example, selective etching may remove one specific material while leaving intact others in proximity. This multi-color challenge gets particularly difficult for selectivity between Si-based materials, as well as between Si and Ge. Instead of plasma activation, this work focused on developing gas-phase spontaneous etch pathways based on thermal chemistry using anhydrous hydrogen fluoride (HF) vapor.

*In situ* spectroscopic ellipsometry experiments discovered substantial spontaneous etching of Si by HF at  $275^\circ\text{C}$ . The Si etch rate was  $12.2 \text{ \AA}/\text{min}$  at an HF pressure of 3 Torr. The Si etch rate increased further with higher HF pressures. In addition, Si etched selectively with an exceptionally high selectivity factor of  $>1,000:1$  versus the retention of  $\text{SiO}_2$  and stoichiometric  $\text{Si}_3\text{N}_4$ .

Temperature-programmed quadrupole mass spectrometry (QMS) experiments confirmed the spontaneous etching of crystalline Si nano-powder by HF.  $\text{SiF}_4$  and  $\text{H}_2$  were observed as the main volatile etch products. QMS detected the  $\text{SiF}_4$  product with a gradual onset above  $\sim 175^\circ\text{C}$ . This temperature dependency indicated that the etch reaction may be limited by  $\text{SiF}_4$  desorption from the Si surface.  $\text{SiF}_4$  desorption from fluorinated Si surfaces has been reported to occur at  $>125^\circ\text{C}$ .

Additional QMS experiments also observed the spontaneous etching of Ge nano-powder by HF.  $\text{GeF}_4$  and  $\text{H}_2$  were revealed as the main volatile etch products. QMS detected  $\text{GeF}_4$  already at  $25^\circ\text{C}$ . The  $\text{GeF}_3^+$  signal intensity increased with elevating temperature and exhibited a maximum at  $\sim 80\text{--}85^\circ\text{C}$ . Subsequently, the  $\text{GeF}_3^+$  signal decreased below the noise level above  $\sim 125^\circ\text{C}$ .

These results suggest that Si etching could be achieved selectively over Ge retention at  $>175^\circ\text{C}$ . Likewise, Ge etching could be accomplished selectively over Si retention at  $<125^\circ\text{C}$ . This reciprocal selectivity between Si and Ge etching will depend on the influence of proximity effects resulting from the volatile etch products when Si and Ge are both present in the reactor.

8:45am **AP1+EM+PS+TF-TuM-4 Theoretically Designed Thermal Atomic Layer Etching Processes for Interconnect Metals**, Miso Kim, H. Cho, Hongik University, Republic of Korea; D. Lee, J. Lee, J. Kim, W. Kim, Hanyang University, Republic of Korea; B. Shong, Hongik University, Republic of Korea  
Atomic layer etching (ALE) is emerging as a key technology for the precise and selective removal of materials at the atomic level, especially for manufacturing of nanoscale three-dimensional semiconductor devices. Previously known thermal ALE processes often involve two-step sequence of surface chemical reactions: surface modification of the substrate such as halogenation, followed by volatilization using another etchant. For example, a recent study reported a thermal ALE process for Ni, employing  $\text{SO}_2\text{Cl}_2$  for halogenation and  $\text{P}(\text{CH}_3)_3$  for volatilization via ligand addition [1]. Since ALE process is based on self-limiting surface chemical reactions, it is desirable to design ALE processes by understanding their surface reactions. However, the mechanistic aspects of such thermal ALE reactions remain significantly underexplored. In this work, we employed neural network potential (NNP) calculations to screen for suitable process conditions for thermal ALE process of metals, especially those considered as materials for nanoscale interconnects. Our findings demonstrate that several metals are capable of forming energetically stable volatile compounds via halogenation and ligand addition of thermal molecular etchants. Several novel thermal ALE processes that were theoretically predicted are experimentally demonstrated with varying etch rates and selectivity between the substrates. Overall our study show the applicability of theoretical analysis of the surface chemical reactions toward design of novel ALE processes.

References. (1) Murdzek, J. A.; Lii-Rosales, A.; George, S. M. Chem. Mater. 2021, 33 (23), 9174–9183.

Acknowledgments. This work was supported by Samsung Electronics.

9:00am **AP1+EM+PS+TF-TuM-5 X-ray Photoelectron Studies of Removal of Sputter Damage from InGaP Surfaces Using Thermal Atomic Layer Etching**, Ross Edel, University of Colorado Boulder; E. Alexander, MIT; A. Cavanagh, University of Colorado Boulder; T. Nam, Soonchunhyang University, Republic of Korea; T. Van Voorhis, MIT; S. George, University of Colorado Boulder

InGaP is widely used for red LED devices. Surface defects on LED devices can lead to non-radiative electron/hole pair recombination that reduces their light output. This light quenching effect is more severe for smaller  $\mu\text{LEDs}$  that have high surface-to-volume ratios. The surface defects are believed to be formed by energetic ion species during plasma processing that forms the  $\mu\text{LEDs}$ . Thermal ALE may provide a method to remove these defects.

To quantify the removal of surface damage, x-ray photoelectron (XPS) studies employed InGaP samples sputtered with argon as a model system. These InGaP samples simulate the  $\mu\text{LED}$  sidewalls that are exposed to energetic species during plasma processing. Thermal InGaP ALE was then performed using static, sequential HF and dimethylaluminum chloride (DMAC) exposures. This procedure yielded etch rates of  $0.5\text{--}1.0 \text{ \AA}/\text{cycle}$  at temperatures from  $300\text{--}330^\circ\text{C}$ , respectively. This work was conducted using a new apparatus that combines a hot wall ALD/ALE reactor with *in vacuo* Auger spectroscopy to allow sample characterization without exposure to air.

InGaP samples damaged by  $\text{Ar}^+$  ion sputtering were analyzed using *ex situ* X-ray photoelectron spectroscopy (XPS) before and after thermal ALE by tracking the shifted components in the P 2p region that correspond to sputter damage. An *ex situ* XPS scan of a sputtered InGaP sample displayed two shifted doublets (Figure 1a) while an unsputtered sample showed only a bulk doublet (similar to Figure 1b). DFT simulations identified the higher energy doublet as phosphorus directly bound to three-coordinate indium or gallium and the lower energy doublet as three-coordinate phosphorus (Figure 2a). In contrast, the DFT simulations showed only a bulk doublet for InGaP without under-coordinated surface atoms (Figure 2b).

InGaP ALE can then remove the XPS features associated with the damaged lattice. A bulk-like XPS spectrum showing minimal damage was recovered after 50 ALE cycles for a sample initially exposed to 500 eV sputtering (Figure 1b). By contrast, annealing for 72 hours at  $300^\circ\text{C}$  without etching was not sufficient to eliminate the damage. AES analysis similarly showed that the argon implanted in the sample by sputtering was removed after etching but not annealing. Increasing the sputtering ion energy to 2 keV required more extensive etching to remove the sputter damage. In this case, 100 ALE cycles were able to largely remove the surface defects. The corresponding AES data showed a linear decrease in implanted argon and reached zero after 100 ALE cycles. The etch depth consistent with 100 ALE cycles indicates a damaged material depth of  $\sim 4 \text{ nm}$ .

# Tuesday Morning, November 5, 2024

9:15am **AP1+EM+PS+TF-TuM-6 Chemical Vapor Etching or Atomic Layer Etching of ZnO? in Situ Ellipsometry and Mass Spectrometric Studies**, *Terrick McNealy-James, S. Berriel, B. Butkus, P. Banerjee*, University of Central Florida

"Atomic layer etching (ALE) stands out as a remarkable technique for precise Angstrom-level control for material removal. With a growing demand in the semiconductor and nanotechnology sectors, ALE becomes a promising solution to address evolving challenges in patterning and in the shrinking of device dimensions. For ideal ALE, processes must demonstrate self-limiting, dose independent etch behavior with well-defined temperature windows. These set of criteria are a challenge for many recently demonstrated metal oxide films.[1]

Here we present the etching characteristics of zinc oxide (ZnO) films, using H<sub>2</sub> and O<sub>2</sub> plasma[2]. We comprehensively map the etch rates using *in situ* spectroscopic ellipsometry. The chemistry of the etching process is verified using mass spectrometry. Etch rate per cycle (EPC) is optimized within a temperature window of 220 – 280 °C. However, it is found that the etch rates are dose dependent and are not only governed by the H<sub>2</sub> pulse times but also by a subsequent "hold" step which continues to etch the ZnO film with no signs of self-limiting behavior. In this context, the H<sub>2</sub> + O<sub>2</sub> plasma process appears to be a controllable chemical vapor etch process.

The impact of inserting etch stop layers in ZnO is explored. While a single monolayer of Al<sub>2</sub>O<sub>3</sub> slows the EPC, 3 monolayers of Al<sub>2</sub>O<sub>3</sub> are sufficient to completely block further etching. These results point to the non self-limiting behavior of H<sub>2</sub> etching of ZnO and strategies which may provide EPC control and selectivity with ZnO composition tuning.

References:

(1) Jonathan L. Partridge, Jessica A. Murdzek, Virginia L. Johnson, Andrew S. Cavanagh, Andreas Fischer, Thorsten Lill, Sandeep Sharma, and Steven M. George  
Chemistry of Materials 2023 35 (5), 2058-2068

(2) A. Mameli, M. A. Verheijen, A. J. M. Mackus, W. M. M. Kessels, and F. Roozeboom, ACS Appl. Mater. Interfaces, vol. 10, 38588, (2018).

9:30am **AP1+EM+PS+TF-TuM-7 Examination of Atomic Layer Etch Mechanisms by Nuclear Magnetic Resonance Spectroscopy**, *Taylor G. Smith, J. Chang*, University of California, Los Angeles **INVITED**

As atomic layer etching (ALE) becomes more widespread, there is a need to better understand the underlying mechanisms by which it operates. Of particular interest is the removal half-cycle of thermal ALE wherein a vapor-solid reaction leads to the formation of a volatile etch product. Solid state magic angle spinning nuclear magnetic resonance (MAS-NMR) can provide a wealth of structural and chemical information, but it has not yet been used to examine ALE reaction mechanisms. In this work, MAS-NMR of CuO etched in solution phase formic acid (FA) is demonstrated and compared with prior density functional theory results<sup>1</sup>. Although it may seem a simple system, the paramagnetic nature of CuO and the formation of many products with slightly different structures both lead to complicated NMR spectra. The issue of significant peak broadening by paramagnetic relaxation can be alleviated in part by spinning at very fast speeds (>30kHz). From the resulting spectra, confirmation of Cu(HCOO)<sub>2</sub>·4H<sub>2</sub>O as a product is possible by comparison to a commercial reference powder. However, assignment of other peaks requires correlation spectroscopy showing <sup>13</sup>C-<sup>13</sup>C and <sup>1</sup>H-<sup>13</sup>C correlations to deduce the structures of the various products, illuminating the reaction landscape of CuO with FA. To extend these findings to the vapor-solid interactions present in ALE, a special heterogeneous NMR rotor can be used that was originally designed for use with high pressure gases. To adapt this rotor use with lower pressure FA vapor, a novel rotor packing method that separates the FA from the CuO prior to vaporization is presented.

**Atomic Scale Processing Mini-Symposium**

**Room 116 - Session AP2+EM+PS+TF-TuM**

**Atomic Layer Etching II: Energy-Enhanced Processes**

**Moderators: Steven M. George**, University of Colorado at Boulder, **Austin Minnich**, California Institute of Technology

11:00am **AP2+EM+PS+TF-TuM-13 Atomic Layer Etching of Lithium Niobate for Quantum Photonics**, *Austin Minnich*, California Institute of Technology **INVITED**

Lithium niobate (LiNbO<sub>3</sub>, LN) is a ferroelectric crystal of interest for integrated photonics owing to its large second-order optical nonlinearity and the ability to impart periodic poling via an external electric field. However, on-chip device performance based on thin-film lithium niobate (TFLN) is presently limited by optical loss arising from corrugations between poled regions and sidewall surface roughness. Atomic layer etching (ALE) could potentially smooth these features and thereby increase photonic performance, but no ALE process has been reported for LN. Here, we report a directional ALE process for x-cut MgO-doped LN using sequential exposures of H<sub>2</sub> and SF<sub>6</sub>/Ar plasmas. We observe etch rates up to 1.01 +/- 0.05 nm/cycle with a synergy of 94%. We also demonstrate ALE can be achieved with SF<sub>6</sub>/O<sub>2</sub> or Cl<sub>2</sub>/BCl<sub>3</sub> plasma exposures in place of the SF<sub>6</sub>/Ar plasma step with synergies above 90%. When combined with a wet post-process to remove redeposited compounds, the process yields a 50% decrease in surface roughness. With additional optimization to reduce the quantity of redeposited compounds, these processes could be used to smoothen surfaces of TFLN waveguides etched by physical Ar<sup>+</sup> milling, thereby increasing the performance of TFLN nanophotonic devices or enabling new integrated photonic capabilities.

11:30am **AP2+EM+PS+TF-TuM-15 Tunable Electron Enhanced Etching of β-Ga<sub>2</sub>O<sub>3</sub> Using HCl Reactive Background Gas and Positive Sample Voltage**, *Michael Collings*, University of Colorado Boulder; *J. Steele, D. Schlom, H. Xing*, Cornell University; *S. George*, University of Colorado Boulder

Crystalline β-Ga<sub>2</sub>O<sub>3</sub> is an ultra-wide band gap material with important applications for high power electronics. High precision etching is required for β-Ga<sub>2</sub>O<sub>3</sub> device fabrication. Previous thermal atomic layer etching (ALE) attempts to etch β-Ga<sub>2</sub>O<sub>3</sub> have not been successful. Plasma etching of β-Ga<sub>2</sub>O<sub>3</sub> using Cl-containing gases is difficult for Ångstrom-level etching control and can leave surface damage. In this work, electron-enhanced etching of β-Ga<sub>2</sub>O<sub>3</sub> is performed using a HCl reactive background gas (RBG) and positive sample bias. The β-Ga<sub>2</sub>O<sub>3</sub> is a -oriented epitaxial film grown by suboxide molecular-beam epitaxy on a single-crystal (0001) Al<sub>2</sub>O<sub>3</sub> substrate. The ~100 eV primary electrons from a hollow cathode plasma electron source (HC-PES) are incident on the β-Ga<sub>2</sub>O<sub>3</sub> sample. The HC-PES is a chemically robust electron source capable of delivering >200 mA over an area >10 cm<sup>2</sup>. The HCl reactive background gas (RBG) is present at ~1 mTorr. A small positive voltage of <50 V is applied to the sample stage.

The β-Ga<sub>2</sub>O<sub>3</sub> film thickness was monitored using *in situ* spectroscopic ellipsometry during electron exposure. Figure 1 shows that the etching of β-Ga<sub>2</sub>O<sub>3</sub> is tunable from 1-50 Å/min by varying the stage voltage from 0 to +40 V, respectively. No etching was monitored from electron exposures without the HCl RBG. Negligible etching was observed without a positive sample stage. The following mechanism can explain these results: (1) The primary electrons at ~100 eV can generate secondary electrons from the substrate. (2) The lower energy secondary electrons can attach to the HCl gas in the reactor. (3) The electron attachment then dissociates HCl into H + Cl<sup>-</sup> through dissociative electron attachment ionization. (4) The Cl<sup>-</sup> negative ions are attracted to the sample by the positive sample stage voltage. (5) The incoming Cl<sup>-</sup> flux leads to an enhancement in etch rate resulting from the formation of volatile chloride species. An illustration of this proposed mechanism is shown in Figure 2.

The β-Ga<sub>2</sub>O<sub>3</sub> etching was reproducible and only weakly dependent on the primary electron energy from 100-150 eV. The electron current going to ground through the sample also increased with positive sample voltages as expected if the secondary electrons are pulled back to the sample. Surface morphology of the β-Ga<sub>2</sub>O<sub>3</sub> was also investigated after the electron enhanced etching. The RMS roughness decreased after etching. The RMS roughness decreased from 1.88 nm to 1.58 nm after the etching process removed 10 nm at +10 V stage voltage. In contrast, the surface roughness did not change after only electron exposures in the absence of HCl RBG.

# Tuesday Morning, November 5, 2024

11:45am **AP2+EM+PS+TF-TuM-16 Bias-Pulsed Atomic Layer Etching**, *Julian Michaels*, University of Illinois at Urbana-Champaign; *N. Deegan*, Argonne National Laboratory, USA; *Y. Tsaturyan*, University of Chicago; *R. Renzas*, University of Nevada Reno; *G. Eden*, University of Illinois at Urbana-Champaign; *D. Awschalom*, University of Chicago; *J. Heremans*, Argonne National Laboratory, USA

Atomic layer etching (ALE) is a binary cyclical process noted for its ability to controllably remove atomic monolayers for nanotechnological device fabrication; however, its relatively slow effective etch rate, often less than a monolayer each minute (tenths of an Angstrom per second), limits its applicability to niche devices that necessitate unmatched precision. If the process were slightly faster, semiconductor, optical, and quantum devices would be regularly implementing ALE because it can reach critical dimensions more consistently while simultaneously offering a smoother post-etch surface, both of which deliver superior device performance regardless of the application.

ALE is slow because the chemical reagent gas(es) is purged in and out of the chamber during each cycle. This is standard practice so that the binary steps, chemical and physical, are fully separated, but purge steps also tend to be the most time-consuming components of any ALE process. Thus, if shortening the cycle duration (speeding up the effective etch rate) is the aim, minimizing purge step duration is a sensible first pursuit.

Bias-pulsed atomic layer etching (BP-ALE) is the execution of the above goal with plasma etching in perhaps the simplest way possible. While traditional plasma ALE often pulses gas flows, plasma DC bias, chamber pressure, substrate temperature, and other parameters, BP-ALE achieves atomic precision by pulsing merely the plasma DC bias, hence “bias-pulsed” indicates that the plasma DC bias is the only parameter that distinguishes the steps, and the purge step duration is absolutely minimized as there is no gas purging whatsoever.

As of now, BP-ALE has been demonstrated in both 4H-SiC and diamond, where the usual ALE cycle duration that often exceeds a minute is superseded by the 6-second cycles of BP-ALE, and smoothing to subangstrom RMS surface roughness is achieved for both after etch treatment. This talk seeks to outline the main differences between BP-ALE in execution and potential applications, explain the material and chemistry characteristics needed for a viable BP-ALE method, and predict material/chemistry systems that are suitable for BP-ALE processing.

12:00pm **AP2+EM+PS+TF-TuM-17 Atomic Layer Etching of 2D Transition Metal Dichalcogenides Semiconductors and Its 2D Device Application**, *Jeongmin Kim, J. Kim*, Seoul National University, Republic of Korea

Transition metal dichalcogenides (TMDs), a class of 2D materials, possess a layered structure with individual layers bound by van der Waals forces. TMDs exhibit excellent electrical properties and have potential applications in various fields due to their low surface defect density. Moreover, TMDs possess a unique property where the bandgap varies with the number of layers, leading to changes in electrical characteristics depending on the thickness. Therefore, precise control of TMD thickness is crucial. Conventional etching methods, such as reactive ion etching, suffer from plasma-induced damage or difficulties in precise thickness control, making them unsuitable for accurate thickness control of TMDs. Consequently, atomic layer etching (ALE) utilizing self-limiting reactions has been devised to achieve precise thickness control at the atomic level.

We developed an ALE process for TMDs utilizing the adsorption of SF<sub>6</sub> gas, which exhibits minimal reactivity at room temperature. In a capacitively coupled plasma system, an etching with constant-thickness for each cycle was achieved by adsorbing SF<sub>6</sub> followed by Ar<sup>+</sup> ion bombardment at an appropriate radio frequency (RF) power. The etch rate was controllable, and no change in the etching rate was observed within a specific RF power range. This was realized by the self-limiting reaction induced by the decomposition of SF<sub>6</sub> under Ar<sup>+</sup> ion bombardment where further sputtering does not occur once all of the adsorbed SF<sub>6</sub> molecules are consumed. Using our ALE process, TMD-based recessed-channel FETs were fabricated. The electrical characteristics and device performance were evaluated, showing a decrease in off-current with reduced channel thickness and no significant deterioration in device performance. This ALE method enables precise thickness control while maintaining the crystallinity of the channel in TMD-based electronic devices, contributing to device performance enhancement. The ALE technology developed in this study paves the way of the advanced application with the TMD-based electronic devices.

This work was supported by the Korea Research Institute for defense Technology planning and advancement (KRIT) grant funded by Defense Acquisition Program Administration (DAPA) (KRIT-CT-21-034)

## Atomic Scale Processing Mini-Symposium Room 116 - Session AP+PS+TF-TuA

### Atomic Layer Etching III: Plasma Processes

Moderators: Robert Bruce, IBM Research, T. J. Watson Research Center, Udyavara Sagar, Lam Research

2:15pm AP+PS+TF-TuA-1 Atomic Layer Etching with Plasma Processing for Semiconductor Device Fabrication, **Heeyeop Chae**, Sungkyunkwan University (SKKU), Republic of Korea

INVITED

The critical dimensions of semiconductor devices are continuously shrinking in nanometer and atomic scale with 3D device structure. The demand for dimension control in angstrom level is drastically increasing also in etching processes. Atomic layer etching (ALE) processes are being actively studied and developed for various metals, semiconductor, and dielectric materials. In this talk, plasma processes for atomic layer etching will be discussed for both isotropic and anisotropic patterning of metals and dielectric materials including molybdenum, ruthenium, cobalt, titanium nitride, tantalum nitride, hafnium oxide, zirconium oxides. [1-9] Typical ALE processes consist of surface a modification step and a removal step. For the surface modification, various fluorination, chlorination and oxidation schemes were applied including fluorocarbon deposition, halogenation, oxidation with radicals generated plasmas. For the removal or etching step, various schemes were applied including ion-bombardment, heating, ligand volatilization, ligand exchange, and halogenation. The surface characteristics such as surface roughness and surface residue after plasma-enhanced ALE processes will be also discussed.

- 1) K. Koh, Y. Kim, C.-K. Kim, H. Chae, *J. Vac. Sci. Technol. A*, 36(1), 10B106 (2017)
- 2) Y. Cho, Y. Kim, S. Kim, H. Chae, *J. Vac. Sci. Technol. A*, 38(2), 022604 (2020)
- 3) Y. Kim, S. Lee, Y. Cho, S. Kim, H. Chae, *J. Vac. Sci. Technol. A*, 38(2), 022606 (2020)
- 4) D. Shim, J. Kim, Y. Kim, H. Chae, *J. Vac. Sci. Technol. B.*, 40(2) 022208 (2022)
- 5) Y. Lee, Y. Kim, J. Son, H. Chae, *J. Vac. Sci. Technol. A.*, 40(2) 022602 (2022)
- 6) J. Kim, D. Shim, Y. Kim, H. Chae, *J. Vac. Sci. Technol. A.*, 40(3) 032603 (2022)
- 7) Y. Kim, H. Chae, *Appl. Surf. Sci.*, 619, 156751 (2023)
- 8) Y. Kim, H. Chae, *Appl. Surf. Sci.*, 627, 157309 (2023)
- 9) Y. Kim, H. Chae, *ACS. Sustain. Chem. Eng.*, 11, 6136 (2023)

2:45pm AP+PS+TF-TuA-3 Atomic Layer Etching in HBr/He/Ar/O<sub>2</sub> Plasmas, **Qinzhao Hao**, M. Elgarhy, University of Houston; P. Kim, S. Nam, S. Kang, Samsung Electronics Co., Republic of Korea; V. Donnelly, University of Houston

Atomic layer etching (ALE) of Si is reported in a radio frequency (RF) pulsed-power inductively-coupled plasma (ICP), with periodic injections of HBr into a continuous He/Ar carrier gas flow, sometimes with trace added O<sub>2</sub>. Several pulsing schemes were investigated, with HBr injection simultaneous with or alternating with ICP power. The product removal step was induced by applying RF power to the substrate, in sync with ICP power. Etching and dosing were monitored with optical emission spectroscopy. Little or no chemically-enhanced ion-assisted etching was observed unless there was some overlap between HBr in the chamber and ICP power. This indicates that HBr dissociative chemisorption deposits much less Br on Si, compared with that from Br created by dissociation of HBr in the ICP. Chemically-assisted etching rates nearly saturate at 2.0 nm/cycle as a function of increasing HBr-containing ICP dose at -75 V<sub>DC</sub> substrate self-bias. The coupled effects of O<sub>2</sub> addition and substrate self-bias DC voltage on etching rate were also explored. Etching slowed or stopped with increasing O<sub>2</sub> addition. As bias power was increased, more O<sub>2</sub> could be added before etching stopped.

3:00pm AP+PS+TF-TuA-4 Comparisons of Atomic Layer Etching of Silicon in Cl<sub>2</sub> and HBr-Containing Plasmas, **Mahmoud Elgarhy**, Q. Hao, University of Houston; P. Kim, S. Nam, S. Kang, Samsung Electronics Co.; V. Donnelly, University of Houston

This talk will report an experimental investigation of Cl<sub>2</sub> vs. HBr for plasma atomic layer etching (ALE) of silicon. An inductively coupled plasma (ICP) source with a constant flow of Ar (and sometimes He) carrier gases, and

HBr or Cl<sub>2</sub> as a dosing gas was used for etching Si (100) samples. Optical emission spectroscopy was used to follow relative yields of SiCl, SiCl<sub>2</sub>, SiBr and SiBr<sub>2</sub>, and scanning electron microscopy and profilometry were used to measure etching rates. HBr and Cl<sub>2</sub> residence times in the chamber were determined by measuring time-resolved pressure during gas dosing. It was found that the pressure rise and fall times were much longer for HBr compared to Cl<sub>2</sub>, suggesting that HBr hangs up on the chamber wall after gas dosing. The effect of the delay time between gas dosing and the start of ICP power on the etching rate was also investigated. When HBr or Cl<sub>2</sub> were injected into the reactor with the plasma on, etching occurs for both sources, with Cl<sub>2</sub> having a higher etching rate. When HBr or Cl<sub>2</sub> were fed to the reactor with the plasma off, only Cl<sub>2</sub> etches. This indicates that the HBr does not chemisorb on Si, and bromination of the surface requires the plasma to form Br atoms, which do adsorb.

3:15pm AP+PS+TF-TuA-5 Atomic Layer Etching of Crystalline MoS<sub>2</sub> by Plasma Fluorination and Oxygenation, **Sanne Deijkers**<sup>1</sup>, C. Palmer, N. Chittock, E. Kessels, A. Mackus, Eindhoven University of Technology, The Netherlands

Molybdenum disulfide (MoS<sub>2</sub>) is a two-dimensional (2D) transition metal dichalcogenide (TMD) with applications in catalysis and nanoelectronics.<sup>1-3</sup> To enable integration of 2D materials in nanoelectronics, highly controlled and low-damage etching processes are required. One example of such a process is the atomic layer etching (ALE) of WSe<sub>2</sub>.<sup>4</sup> In this work, we present a plasma ALE process to etch crystalline MoS<sub>2</sub>. The process involves plasma fluorination and oxygenation, targeting Mo-O-F as a volatile species. Previous work using the approach of fluorination and oxygenation involved thermal chemistries with an etch-per-cycle (EPC) of 0.5 Å for amorphous films and 0.2 Å for crystalline films.<sup>5</sup> As plasmas are more reactive than their gaseous counterparts, they are expected to allow for etching crystalline materials.

Fluorination was performed by a SF<sub>6</sub>-based plasma, and as removal step various oxygen sources were tested. To avoid continuous etching of the MoS<sub>2</sub>, the plasma composition of the fluorination step had to be optimized.<sup>6</sup> Addition of H<sub>2</sub> to the plasma mixture reduces F radical concentration by creating HF species *in situ*.<sup>7</sup> With an adequate H<sub>2</sub> content using a ratio of SF<sub>6</sub>:(SF<sub>6</sub>+H<sub>2</sub>) < 0.3, continuous etching is suppressed, and only modification of the top surface takes place. As second half-cycle, H<sub>2</sub>O, O<sub>2</sub> gas and O<sub>2</sub> plasma exposures were tested. Of these only an O<sub>2</sub> plasma resulted in etching, while dosing H<sub>2</sub>O or O<sub>2</sub> gas resulted in no measurable thickness change. Raman measurements showed a strong decrease in the characteristic E<sub>12g</sub> and A<sub>1g</sub> peaks, indicating etching of crystalline MoS<sub>2</sub>. The complete ALE recipe with saturated SF<sub>6</sub>-based plasma and O<sub>2</sub> plasma exposures had an EPC of 1.1 ± 0.2 Å at 300 °C table temperature.

1. Cao, Y. *ACS Nano* **15**, 11014–11039 (2021).
2. Mahlouji, R. *et al. Adv. Electron. Mater.* **8**, (2022).
3. Deijkers, J. H. *et al. Adv. Mater. Interfaces* **4–9** (2023).
4. Nipane, A. *et al. ACS Appl. Mater. Interfaces* **13**, 1930–1942 (2021).
5. Soares, J. *et al. Chem. Mater.* **35**, 927–936 (2023).
6. Xiao, S. *et al. Sci. Rep.* **6**, 1–8 (2016).
7. Hossain, A. A. *et al. J. Vac. Sci. Technol. A* **41**, (2023).

4:00pm AP+PS+TF-TuA-8 A Reduced Order Model of Plasma-Surface Interactions in Atomic Layer Etching, **David Graves**, Princeton University; J. Vella, TEL Technology Center, America, LLC

Any future physics-based, rather than purely data-driven, digital twin of a plasma tool and process will need a reduced order model (ROM) of the effects of the plasma on the surface being processed. In this talk, I present one possible version of a ROM for simulating a plasma atomic layer etching (ALE) process. The ROM is based on a transient version of a surface site balance model that was first applied in the 1980s for plasma etching. Classical molecular dynamics (MD) simulations of ALE of Si using Cl<sub>2</sub>/Ar<sup>+</sup> cycles are first validated with experimental measurements and then used to provide values for parameters (e.g., ion energy dependent etch yields) for a transient site balance model of the process. The ROM is computationally much faster than the MD simulations and is shown to reproduce additional, and previously unexplained, experimental results. Future applications of MD to plasma-surface interactions in semiconductor device fabrication will likely use another type of ROM. MD methods require interatomic potentials or force fields for all simulated atomic interactions. The force field

<sup>1</sup> TFD James Harper Award Finalist

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parameters can be inferred from higher level methods such as density functional theory (DFT), coupled with neural net data-driven algorithms. I will conclude with preliminary results using one such approach, namely Deep Potential MD (DeePMD), to develop illustrative force fields.

## 4:15pm AP+PS+TF-TuA-9 Atomic Layer Etching of SiO<sub>2</sub> using Sequential Exposures of Al(CH<sub>3</sub>)<sub>3</sub> and H<sub>2</sub>/SF<sub>6</sub> Plasma, *David Catherall, A. Hossain, A. Minnich*, California Institute of Technology

On-chip photonic devices based on SiO<sub>2</sub> are of interest for applications such as microresonator gyroscopes and microwave sources. Although SiO<sub>2</sub> microdisk resonators have achieved quality factors exceeding one billion, this value remains an order of magnitude less than the intrinsic limit due to surface roughness scattering. Atomic layer etching (ALE) has potential to mitigate this scattering because of its ability to smooth surfaces to sub-nanometer length scales. While isotropic ALE processes for SiO<sub>2</sub> have been reported, they are not generally compatible with commercial reactors, and the effect on surface roughness has not been studied. Here, we report an ALE process for SiO<sub>2</sub> using sequential exposures of Al(CH<sub>3</sub>)<sub>3</sub> (trimethylaluminum, TMA) and Ar/H<sub>2</sub>/SF<sub>6</sub> plasma. We find that each process step is self-limiting, and that the overall process exhibits a synergy of 100%. We observe etch rates up to 0.58 Å per cycle for thermally-grown SiO<sub>2</sub> and higher rates for ALD, PECVD, and sputtered SiO<sub>2</sub> up to 2.38 Å per cycle. Furthermore, we observe a decrease in surface roughness by 62% on a roughened film. The residual concentration of Al and F is around 1-2%, which can be further decreased by O<sub>2</sub> plasma treatment. This process could find applications in smoothing of SiO<sub>2</sub> optical devices and thereby enabling device quality factors to approach limits set by intrinsic dissipation.

## 4:30pm AP+PS+TF-TuA-10 Atomic Layer Etching of Cu Using Alternating Cycles of Hexafluoroacetylacetone and O<sub>2</sub> Plasma, *Yusuke Nakatani*, Hitachi High-Tech, Japan; *A. Kaye*, Colorado School of Mines, USA; *Y. Sonoda, M. Tanaka, K. Maeda*, Hitachi High-Tech, Japan; *S. Agarwal*, Colorado School of Mines, USA

Atomic layer etching (ALE) is a critical technology in semiconductor device fabrication, including for interconnect metals such as Cu and Co. Previously, thermal ALE of Cu has been reported using alternating half-cycles of hexafluoroacetylacetone (hfach) and O<sub>2</sub> or O<sub>3</sub> at ~275 °C. It has also been shown that hfach cannot spontaneously etch Cu, and peroxidation of the Cu surface is required. In this presentation, we will report on ALE of Cu at a much lower temperature of 150 °C using hfach and O<sub>2</sub>/Ar plasma half-cycles.

The ALE process was monitored using in situ reflection-absorption infrared spectroscopy (RAIRS). Prior to ALE, the Cu wafers were cleaned using a H<sub>2</sub> plasma at a temperature of 300 °C to reduce the native oxide, and to remove the surface carbonates and adsorbed hydrocarbons. Initially, we tested the reactivity of hfach at 150 °C with a reduced Cu surface, and after re-oxidation with an O<sub>2</sub> plasma. In both cases, in the infrared spectra, we observed absorption bands related to CF<sub>3</sub> (1240 cm<sup>-1</sup>), C=C, and C=O (1645 cm<sup>-1</sup>) vibrations. On a reduced Cu surface, the C=C and C=O bands were much weaker indicating decomposition of hfach. Since hfach does not spontaneously etch Cu, this indicates that an oxidized Cu surface is required for the adsorption of hfach. Our infrared data also show that the ALE window is very narrow, and the etch rate could only be measured at 125 and 150 °C. At temperatures lower than 125 °C, our infrared data shows that hfach does adsorb onto the CuOx surface, but the temperature is likely too low for the formation of the etch products— Cu(hfach)<sub>2</sub> and H<sub>2</sub>O. The subsequent O<sub>2</sub> plasma half-cycle simply removes the hfach ligand and oxidizes the surface further. At 150 °C, a balance is established between surface oxidation and removal of CuOx from the surface as Cu(hfach)<sub>2</sub> and H<sub>2</sub>O. The etch per cycle at 125 and 150 °C were 0.1 and 0.7 Å, respectively. At temperatures higher than 150 °C, atomic force microscopy shows that the Cu surface roughens due to severe oxidation, and the Cu film thickness cannot be measured with ellipsometry.

## 4:45pm AP+PS+TF-TuA-11 Enabling Anisotropic and Selective Etch Through Surface Modification of Ru, *Owen Watkins*, UCLA; *H. Simka*, Samsung Electronics; *J. Chang*, UCLA

Ruthenium is a potential replacement for copper in metal interconnects below 10 nm, where the grain boundary scattering and the need for a barrier layer increases the effective resistivity of Cu. Unlike Cu, Ru can be directly etched using O<sub>2</sub>-plasma-based processes, allowing a subtractive metal patterning to be used. Current Ru etching processes largely rely on O<sub>2</sub>/Cl<sub>2</sub>-based RIE. While this process is able to anisotropically etch Ru, it requires Cl<sub>2</sub> and damages the hard mask, resulting in ballooning and low selectivity. A cyclic process that is halogen-free, anisotropic, and selective has been proposed. The process consists of a nitrogen plasma passivation

step, hydrogen plasma reduction step, and oxygen plasma etching step. The passivating layer of RuN formed by N<sub>2</sub> plasma exposure can be reduced in H<sub>2</sub> plasma. Bias applied to the substrate during the H<sub>2</sub> step results in the selective reduction of RuN on the vertically-exposed surface, leaving a layer of RuN on the sidewalls. During the O<sub>2</sub> plasma step, RuN passivates the sidewall from O radicals that would otherwise etch the sidewall. The two surface modification steps cause the normally isotropic O<sub>2</sub> plasma etch to become anisotropic, while maintaining a high selectivity vs. SiO<sub>2</sub> and SiN used as the hard mask. The sequential process has been experimentally shown to be anisotropic and selective, and results in lower resistivity and surface roughness vs. O<sub>2</sub> plasma alone. To understand the effects of the surface modification steps on the overall process, each step of the sequential process has been examined, including the surface composition and structure of the Ru film after each plasma exposure. RuO<sub>2</sub> and RuN thin films were deposited as references, allowing the presence of RuN after nitridation to be confirmed using XPS and XRD. The etch rate of nitridated Ru films was found to be 0.4 nm per minute in O<sub>2</sub> plasma, more than 15 times less than the etch rate of Ru in O<sub>2</sub> plasma at the same conditions. Removal of the N<sub>2</sub> plasma step from the process resulted in isotropic etching, confirming that nitridation is responsible for sidewall passivation. XPS was used to confirm that most, but not all of the RuN surface layer is reduced after exposure to H<sub>2</sub> plasma. H<sub>2</sub> plasma was also found to significantly affect the etching of hard mask SiO<sub>2</sub>. Reduction of the plasma density by lowering the power and increasing the pressure was necessary to reduce SiO<sub>2</sub> etching and corner faceting during the H<sub>2</sub> step. The combination of surface modification techniques results in a process that has been demonstrated for features down to 32 nm pitch.

## 5:00pm AP+PS+TF-TuA-12 Enhanced Control of Plasma Surface Interaction to Etch Alloys Using Transient Assisted Plasma Etching (TAPE), *Atefeh Fathzadeh*, KU Leuven/IMEC, Belgium; *P. Bezard*, IMEC Belgium; *T. Conard, F. Holsteyns*, IMEC, Belgium; *S. De Gendt*, KU Leuven/Imec, Belgium

A novel plasma process design called transient-assisted plasma process (TAPP) has been recently introduced to tackle multiple patterning challenges brought by the introduction of 3D devices, new ultra-thin films, and compound materials without suffering from the poor throughput of Atomic layer etching. In the realm of dry-etching, it has exhibited promising patterning capabilities at etch rates compatible with high-volume manufacturing. In deposition applications, it also has demonstrated superior control over precursor dosage and fragmentation for in-situ hard-mask deposition compared to conventional methods. Moreover, from a sustainability perspective, Transient-assisted processing (TAP) presents considerable advantages by notably reducing the consumption of problematic gases. TAPE operates in cycles, involving at least two phases: Time-limited injection of the reactant (with or without plasma), and when the injection is stopped, a gas transient happens in the plasma, where the reactant concentration diminishes over time, as shown in Figure 1. The fluence of reactive species is regulated by the gas pulse characteristics (partial pressure, etc.) and its associated plasma transient, while ion fluence is governed by the duration of the plasma phase. This segregation yields significantly enhanced control over plasma-surface interactions compared to conventional plasma etching techniques. This design is compatible with any gas mixture, and energy sources (ions, photons, electrons, fast neutral species/clusters, etc.).

Enhancing control over plasma-surface interactions holds promise in rectifying the uneven etching observed in multicomponent materials like alloys. This imbalance in etching induces a compositional drift, thereby impeding the process and deteriorating material characteristics as shown in Figure 2a. Typically, one component undergoes predominantly chemical etching, while the other experiences primarily physical etching. In TAPE, most chemically-driven etching occurs early during the plasma step when a substantial amount of etchant is present. The modified surface/profile will then be exposed to a reduced etchant quantity and a continued ion bombardment. Each cycle is thus capable of providing the necessary species for a balanced etching of the compound's elements. Figure 2b compares the chemical composition of InGaZnO after conventional etching and TAPE, while Figure 2c compares the etch rate, and profile relative to a previously published ALE process. Meanwhile, TAPE consumes 25 times less CH<sub>4</sub> than the ALE process.

## 5:15pm AP+PS+TF-TuA-13 Leveraging Plasma Nitridation for Atomic Layer Etching of Ni<sub>3</sub>Al, *Taylor G. Smith*, University of California, Los Angeles; *J. de Marneffe*, imec, Belgium; *J. Chang*, University of California, Los Angeles

Extreme ultraviolet (EUV) lithography is entering a new era with high numerical aperture (NA) EUV, increasing the importance of integrating new

# Tuesday Afternoon, November 5, 2024

absorber layer materials like Ni<sub>3</sub>Al to mitigate mask 3D effects. However, Ni<sub>3</sub>Al adoption has been limited by difficulties in anisotropically etching Ni<sub>3</sub>Al with high selectivity to the underlying Ru capping layer. A previously reported ALE based on plasma oxidation was shown effective at etching Ni<sub>3</sub>Al but had poor selectivity to Ru, which etches spontaneously in oxygen plasma. An atomic layer etch (ALE) based on plasma nitridation and formic acid (FA) vapor exposure was previously demonstrated to etch Ni<sup>1</sup>, and in this work the nitridation-based ALE process is extended to the more complex and industrially relevant Ni<sub>3</sub>Al. X-ray photoelectron spectroscopy (XPS) is used to analyze the surface composition of blanket Ni<sub>3</sub>Al films after plasma nitridation, showing the nitrided films have a stoichiometry of Ni<sub>2.4</sub>AlN. The effects of plasma power, from 200 to 700 W, and pressure, from 8 to 50 mTorr, on plasma nitridation are examined, with current results indicating that high power and low pressure lead to the greatest amount of surface nitridation. Langmuir probe measurements are used to correlate these effects with changes in plasma density and electron temperature. For the removal half-cycle, FA vapor was shown to remove the nitride layer as indicated by the disappearance of the characteristic metal nitride peak in the N 1s spectrum at 397.2 eV. XPS also shows depletion of Ni as successive ALE cycles are applied, an effect that can be mitigated using basic etchants due to their selective removal of Al over Ni. Selectivity to Ru is measured by etching blanket Ru films and measuring the thickness with SEM, with a current selectivity of 2.4. To assess anisotropy, Ni<sub>3</sub>Al is first conformally deposited over a patterned Si substrate by physical vapor deposition (PVD), and the samples are subsequently processed by ALE. The ion energy of the nitrogen plasma is varied by changing the voltage applied to an ion extraction grid from -100 to +100 V, with the sidewall Ni<sub>3</sub>Al etch compared to the vertical Ni<sub>3</sub>Al etch using scanning electron microscopy (SEM).

<sup>1</sup> T.G. Smith, A.M. Ali, J.F. de Marneffe, J.P. Chang, *J. Vac. Sci. Technol. A* 42, 022602 (2024).

## Atomic Scale Processing Mini-Symposium

### Room 116 - Session AP1+EM+PS+TF-WeM

#### Energy-Enhanced Atomic Layer Processing

**Moderators:** Ashley Bielinski, Argonne National Laboratory, USA, John F. Conley, Jr., Oregon State University

**8:00am AP1+EM+PS+TF-WeM-1 Low-Temperature Synthesis of Crystalline  $\text{In}_x\text{Ga}_{1-x}\text{N}$  Films via Plasma-Assisted Atomic Layer Alloying,** S. Allaby, F. Bayansal, H. Silva, B. Willis, Necmi Biyikli, University of Connecticut

Based on our first demonstration of crystalline III-nitride film growth via hollow-cathode plasma-assisted atomic layer deposition (HCP-ALD) at substrate temperatures as low as 200 °C, this technique is attracting increasing interest for the low-temperature deposition of various semiconductor layers. Despite its success for binary III-nitride films, ternary III-nitrides pose additional challenges including limitation on fine stoichiometry control, potential incompatibility of plasma gas mixtures, and complexity of in-situ ellipsometry analysis of the growing film. In this work, we share our experimental findings on the self-limiting growth of  $\text{In}_x\text{Ga}_{1-x}\text{N}$  films on  $\text{SiO}_2/\text{Si}$ , quartz, and sapphire substrates using digital alloying technique in an HCP-ALD reactor at 200 °C.

The  $\text{In}_x\text{Ga}_{1-x}\text{N}$  alloy films were deposited using conventional metal-alkyl precursors (triethylgallium, trimethylindium) and two different nitrogen plasmas ( $\text{N}_2/\text{H}_2$ ,  $\text{N}_2/\text{Ar}$ ) as metal precursor and nitrogen co-reactant, respectively. GaN and InN unit ALD cycle parameters have been determined using the saturation curves for each binary compound. Digital alloying technique was used by forming ALD supercycles with the following GaN:InN cycle ratios: (9:1), (6:1), (3:1). The targeted indium concentrations ranged within (10% – 50%) range.  $\text{In}_x\text{Ga}_{1-x}\text{N}$  alloy films with different stoichiometries and thickness values around 50 nm were synthesized to further characterize the structural, chemical, optical, and electrical film properties.

*In-situ* ellipsometry was employed to monitor the surface ligand-exchange reactions and plasma surface interactions. XRD, XRR, XPS, spectroscopic ellipsometer, UV/Vis spectroscopy, and Hall-effect measurements are carried out to characterize the crystal structure, average crystal grain size, film density, stoichiometry (Ga:In ratio), impurity content, complex refractive index, optical bandgap, film resistivity, carrier concentration and electron mobility, respectively. The experimental results will be discussed along with faced challenges, potential solutions and follow-up studies.

**8:15am AP1+EM+PS+TF-WeM-2 Comparison of Low Temperature Methods for Crystallization of Vanadium Oxide Produced by Atomic Layer Deposition,** Peter Litwin, Naval Research Laboratory, USA; M. Currie, N. Nepal, M. Sales, D. Boris, S. Walton, V. Wheeler, US Naval Research Laboratory

Crystalline  $\text{VO}_2$  (c- $\text{VO}_2$ ) undergoes a phase transformation between two crystalline states near room temperature ( $\approx 68$  °C), which is accompanied by a metal-to-insulator transition (MIT). This favorable MIT in stoichiometric c- $\text{VO}_2$  is of interest for numerous applications such as passive thermal regulation (e.g. energy efficient windows), thermal sensors, and passive radio frequency components. Current  $\text{VO}_2$  films deposited by thermal atomic layer deposition (ALD) processes are amorphous and require a high temperature post-deposition annealing step ( $\geq 400$  °C) to crystallize, which often limits the application space of ALD  $\text{VO}_2$  due to thermal budget constraints. Thus, the development of processes to produce ALD c- $\text{VO}_2$  without the need of a high-temperature annealing step are desired.

Two possible routes to c- $\text{VO}_2$  are plasma-enhanced ALD (PEALD) and femtosecond laser processing (fsLP). PEALD offers increased kinetics through the simultaneous delivery of a flux of both energetic and reactive plasma species to the growth surface, allowing for deposition and crystallization at lower processing temperatures. However, the enhanced reactivity of oxidizing-plasma sources poses challenges not present in thermal ALD processes of  $\text{VO}_2$ . For example, the oxidation state of the V in the metal-organic precursor is less of a driver for stoichiometric control often resulting in the more stable  $\text{V}_2\text{O}_5$  with plasma processes. In fsLP, crystallization is initiated as a result of non-equilibrium excited-state dynamics in the film occurring on sub-ps timescales. This produces a combination of athermal and thermal annealing expected to promote the formation of c- $\text{VO}_2$ , even under ambient conditions. Both methodologies maintain sub-200 °C temperature windows which facilitate the use of c- $\text{VO}_2$  in a wider range of applications. For example, high-temperature annealing

of  $\text{VO}_2$  on metal substrates often results in the dewetting of  $\text{VO}_2$  films; both PEALD and fsLP are potential solutions.

Here we report on investigations into the efficacy of PEALD and fsLP to produce c- $\text{VO}_2$ . A focal point of the PEALD studies is correlating plasma properties, including plasma power, Ar/ $\text{O}_2$  ratio, system pressure, and total gas flow during the plasma step, with the control of the  $\text{VO}_x$  stoichiometry and crystallinity. We demonstrate control of the amorphous to crystalline transition as a function of PEALD parameters and comment on control of the  $\text{V}^{4+}/\text{V}^{5+}$  ratio. fsLP is shown effective at producing c- $\text{VO}_2$  from amorphous ALD films under ambient conditions. We also discuss the ability of the technique to produce c- $\text{VO}_2$  on polymer and metal substrates, an application space often incompatible with high-temperature annealing.

**8:30am AP1+EM+PS+TF-WeM-3 Temperature-Dependent Dielectric Function of Plasma-Enhanced ZnO Atomic Layer Deposition using in-Situ Spectroscopic Ellipsometry,** Youssa Traouli, U. Kilić, University of Nebraska-Lincoln, USA; M. Schubert, University of Nebraska - Lincoln; E. Schubert, University of Nebraska-Lincoln, USA

In this study, *in-situ* spectroscopic is employed to real-time monitor the growth of ZnO thin films fabricated by plasma-enhanced atomic layer deposition for different temperatures. The process involves dimethylzinc,  $\text{Zn}(\text{CH}_3)_2$ , organometallic precursor and oxygen plasma as the primary reactant and co-reactant, respectively. We investigate the cyclic surface modifications and growth mechanisms of ZnO for different substrate temperatures. Subsequently, the deposition chamber is then used as an thermal annealing chamber to investigate the evolution of dielectric function of ZnO ultra-thin films for different temperature values ( $22^\circ\text{C} \leq T \leq 300^\circ\text{C}$ ).

Hence, the temperature-dependent complex dielectric function spectra of ZnO ultra-thin film is obtained. Complementary x-ray photoelectron spectroscopy, x-ray diffraction, and atomic force microscopy are also used to provide the compositional, structural, and morphological characteristics of the ZnO films, respectively. These findings highlight the critical role of precise thermal management in ALD processes for tailoring the dielectric properties of ZnO thin films. The insights gained from this study are crucial for the development and optimization of ZnO PE-ALD recipe but also for optoelectronic devices, ensuring enhanced performance and reliability.

**8:45am AP1+EM+PS+TF-WeM-4 Optical Properties and Carrier Transport Characteristics of NiO Films Grown via Low-Temperature Hollow-cathode Plasma-assisted Atomic Layer Deposition,** Fatih Bayansal, S. Allaby, H. Mousa, H. Silva, B. Willis, N. Biyikli, University of Connecticut

While there is an abundance of as-grown unintentionally doped n-type semiconductor materials, only a few alternative materials exhibit p-type conduction without requiring additional high-temperature doping processes. NiO is of particular interest mainly due to its relative stability and promising performance as hole-transport layers in emerging solar cell device structures. However, the stability of film properties including carrier concentration and mobility of NiO needs to be substantially improved for its use as reliable transistor channel layers. While low-temperature thermal, plasma, and ozone-assisted ALD efforts have resulted in NiO films with p-type behavior, degrading film properties over time and at higher temperatures, and low hole mobility values prevent the usage of these layers for devices.

To enhance film properties in low-temperature as-grown NiO layers, our study conducts a comprehensive investigation on plasma-enhanced ALD (PEALD) of NiO films on Si,  $\text{SiO}_2/\text{Si}$ , glass, sapphire, and quartz substrates. This process utilizes nickelocene ( $\text{NiCp}_2$ ) and  $\text{O}_2$  plasmas within a plasma-ALD reactor featuring a stainless steel-based hollow-cathode plasma (HCP) source, equipped with an in-situ ellipsometer. 800-cycle deposition runs at 100 – 250 °C substrate temperatures were carried out to achieve at least 30 nm thick films for further characterization.

The resulting as-grown crystalline (c-NiO) films are characterized for their optical and electrical properties. Films grown at 200 °C exhibited higher refractive index values reaching 2.3, which is in good agreement with reported values for the best polycrystalline NiO films in the literature. NiO films deposited on sapphire and quartz substrates showed strong absorption in the UV region ( $\lambda=190\text{-}380$  nm) yet demonstrated minimal absorption in the visible and near-IR regions. As a result of the analysis using the Tauc relation, it was found that the band gaps of all films were close to the bulk value of 3.6 eV. Furthermore, we will also present the results of Hall-effect measurements conducted at room temperature to determine the film resistivity, type of conduction mechanism, Hall mobility, and carrier concentration. The long-term stability of the NiO films will be investigated at ambient and higher temperature annealing conditions.

# Wednesday Morning, November 6, 2024

9:00am **AP1+EM+PS+TF-WeM-5 Characterizing Inductively Coupled Plasmas in Ar/SF<sub>6</sub> Mixtures for Atomic Layer Deposition, David Boris, V. Wheeler, U.S. Naval Research Laboratory; M. Sales, NRC Research Associateship Program; L. Rodriguez de Marcos, J. Del Hoyo, NASA Goddard Space Flight Center; A. Lang, U.S. Naval Research Laboratory; E. Wollack, M. Quijada, NASA Goddard Space Flight Center; M. Meyer, NRC Research Associateship Program; S. Walton, U.S. Naval Research Laboratory**

Low temperature plasmas containing sulphur hexafluoride (SF<sub>6</sub>) are particularly rich plasmas from the perspective of gas phase chemistry and plasma physics. They possess a wide range of positive and negative ion (SF<sub>x</sub><sup>+</sup>, SF<sub>y</sub><sup>-</sup>, F<sup>-</sup>, F<sub>2</sub><sup>+</sup>, etc.) and reactive neutral species (SF<sub>x</sub>, F, F<sub>2</sub>, etc.) that play important roles in materials processing applications ranging from semiconductor etching [1] to the formation of fluoride based optical thin films [2]. Understanding the physical mechanisms at play in these plasmas is often challenging and requires a comprehensive approach employing multiple diagnostic tools.

In this work, we use a combination of Langmuir probes and optical emission spectroscopy to examine the effects of varying process parameters on the physical characteristics of Ar/SF<sub>6</sub> plasmas generated in a remote, inductively coupled plasma (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 F density, plasma density, plasma potential, and the ratio of positive to negative ions in the plasma. These changes in plasma properties are then tied to changes in the material characteristics of aluminum tri-fluoride (AlF<sub>3</sub>) thin films grown via plasma-enhanced ALD using a remote ICP employing Ar/SF<sub>6</sub> gas mixtures. This work is supported by NASA Astrophysical Research and Analysis (APRA) grant 20-APRA20-0093/ N0017322GTC0044. This work was also partially supported by the NRL Base program through the Office of Naval Research.

[1] D.C. Messina et al, J. Vac. Sci. Technol. A 41, 022603 (2023)

[2] L. V. Rodriguez de Marcos et al, Optical Materials Express 13 (11), 3121-3136 (2023)

9:15am **AP1+EM+PS+TF-WeM-6 Dynamic Global Model of Cl<sub>2</sub>/Ar Plasmas: In-Depth Investigations on Plasma Kinetics, Tojo Rasoanarivo, C. Mannequin, Institut des Matériaux de Nantes Jean ROUXEL - Nantes Université, France; F. Roqueta, M. Boufnichel, ST Microelectronics, France; A. Rhallabi, Institut des Matériaux de Nantes Jean ROUXEL - Nantes Université, France**

Plasma processes such as Atomic Layer Etching (ALE) using Cl<sub>2</sub>/Ar gas mixture are often reported in the literature as chlorine chemistry is suitable for a wide variety of materials [1]. ALE is a cyclic process and Cl<sub>2</sub> and Ar plasmas are implemented for the adsorption and activation steps, respectively, through alternating feedgas overtime or overspace. However, these studies mostly focus on experimental approaches and modeling investigations are scarce. Some others ALE recipes rely on plasma kinetics through specific recipes [2] and to better understand plasma/surface interactions at atomic scale, we must first precisely investigate plasma behavior especially during the switching durations.

In most cases, global models have been well implemented to determine the plasma composition at specific plasma reactor parameters, with good computational time effectiveness [3] in steady-states conditions [4]. We have implemented the dynamic mode to investigate the plasma kinetics during the transitions between the modifying Cl<sub>2</sub> plasma and the Ar activation plasma.

We closely investigate the influence of the switch duration between the Cl<sub>2</sub> to/from Ar feedgas, for different RF powers. We found that under a critical switch duration there is a competition between the plasmas kinetics mainly governed by electrons collisions with the neutrals and the physical residence time depending of the working pressure. For short switch duration from Cl<sub>2</sub> rich plasma toward Ar plasma, we observed discrepancies compared to equivalent steady-state composition on chlorine species. These differences are associated with longer characteristics time reactions than the switch duration. In the case of RF power source switch, we observed for switch duration lower than 100 ms, overshoots of the electron temperature (T<sub>e</sub>). These stiff T<sub>e</sub> variations observed are assumed to originate from quasi-instantaneous electrons acceleration before first collisions with neutrals.

These results may be used to predict plasma behavior during ALE transitions steps or for fast-paced plasma etching processes.

## References

[1] K. J. Kanarik, T. Lill, E. A. Hudson et al., J. Vac. Sci. Technol A: 33, 020 802 (2015).

[2] A. Fathzadeh, P. Bezard, M. Darnon, I. Manders, T. Conard, I. Hofliijk, F. Lazzarino, S. de Gendt, J. Vac. Sci. Technol. A 42, 033006 (2024).

[3] A. Hurlbatt, A. R. Gibson, S. Schröter, J. Bredin, A. P. S. Foote, P. Grondein, D. O'Connell, T. Gans, Plasma Process Polym, 14: 1600138 (2017).

[4] R. Chanson, A. Rhallabi, M. C. Fernandez, C. Cardinaud, J. P. Landesman, J. Vac. Sci. Technol A, A 31, 011301 (2013).

9:30am **AP1+EM+PS+TF-WeM-7 Precise Growth and Removal of Carbon Films by Electron-Enhanced Chemical Vapor Deposition (EE-CVD) and Chemical Vapor Etching (EE-CVE), Z. Sobell, Steven George, University of Colorado at Boulder**

Electron-enhanced chemical vapor deposition (EE-CVD) was used to grow carbon films at T < 70 °C. EE-CVD employs a continuous flux of low energy (~100 eV) electrons that are incident on the sample through a methane (CH<sub>4</sub>) reactive background gas (RBG). Electron-enhanced chemical vapor etching (EE-CVE) was also used to etch carbon films at < 70 °C. EE-CVE employs a continuous flux of low energy electrons that are incident on the sample through an oxygen (O<sub>2</sub>), ammonia (NH<sub>3</sub>), or hydrogen (H<sub>2</sub>) RBG. Both EE-CVD and EE-CVE were accomplished with precise rate control.

The EE-CVD and EE-CVE used an electron beam from a hollow cathode plasma electron source with currents on the sample of ~30 mA over ~10 cm<sup>2</sup>. The electron beam can desorb surface species by electron stimulated desorption. The electron beam also travels through the RBG in the reactor at pressures of ~1-3 mTorr. Electron induced dissociation can form radicals and ions that facilitate the growth or removal of the carbon film. In addition, a negative voltage (-30 V) on the substrate (sample bias) was observed to greatly enhance both the deposition and etching of carbon films. The negative voltage is believed to pull positive ions to the substrate to enhance the growth or removal.

With no applied sample bias, carbon deposition proceeded at ~22 Å/min for a CH<sub>4</sub> flowrate of 10 SCCM (Fig. 1). The introduction of a sample bias of -30 V increased the deposition rate by >20 times to ~480 Å/min. In contrast, carbon deposition with a +30 V sample bias proceeded at a similar rate to carbon deposition with no sample bias. For etching of carbon films with a -30 V sample bias and RBG flow rates of 4 SCCM, O<sub>2</sub> produced the highest carbon etch rate at ~225 Å/min (Fig. 2). In contrast, NH<sub>3</sub> displayed a slower carbon etch rate of ~48 Å/min and H<sub>2</sub> had an even slower carbon etch rate of ~18 Å/min.

Raman spectroscopy was used to characterize the carbon films grown at different sample biases. At negative substrate voltage, the carbon films displayed faster growth, were more disordered (D:G peak ratio=2.29), and exhibited faster etching. At zero substrate voltage, the carbon films displayed slower growth, were more ordered (D:G peak ratio=1.18), and exhibited slower etching.

Many applications are possible for the EE-CVD and EE-CVE of carbon films. More ordered carbon films may find use as hard masks or diffusion barriers. Amorphous carbon films may be employed as channel materials. Carbon hard masks are currently removed with an O<sub>2</sub> plasma which also oxidizes the surrounding and underlying material. Using H<sub>2</sub> and electrons may allow for a single-step oxygen-less hard mask removal.

9:45am **AP1+EM+PS+TF-WeM-8 Microwave Enhanced ALD of Al<sub>2</sub>O<sub>3</sub>, Benjamin Kupp, J. Haglund, S. Witsell, J. Conley, Oregon State University**

The low deposition temperatures typical of ALD are advantageous for many applications. However, low deposition temperatures can allow incorporation of -OH groups or residual impurities from unreacted ligands which can lead to non-ideal stoichiometry and sub-optimal physical, optical, and electrical properties. Although increasing the deposition temperature and post deposition annealing can both help drive off impurities and improve film properties, the temperatures required may (i) move a process out of the ALD regime or (ii) exceed the thermal budget, respectively. To maintain a low ALD temperature while maximizing film properties, adding energy in-situ during each ALD cycle or supercycle can help drive/speed reactions and reduce impurity incorporation. For example, including rapid thermal annealing as part of the ALD cycle have been shown to improve density, stoichiometry, electrical, and optical properties that cannot be achieved by post deposition annealing alone [1-4]. Other reported in-situ energy enhanced EE-ALD methods include flash lamp annealing, plasma, UV, and laser exposure, electric fields, and electron-beams [5-15]. Here, we introduce microwave enhanced MWE-ALD.

Al<sub>2</sub>O<sub>3</sub> films were deposited at 300 °C using TMA and H<sub>2</sub>O in a Picosun R200 PE-ALD chamber integrated with a custom microwave antenna and an MKS SG 1024 solid state microwave (MW) generator. Film thickness and

refractive index,  $n$ , were modeled using a Film Sense FS-1 mapping ellipsometer. A 30 s in-situ 400 W MW exposure (*without* plasma generation) during either the TMA or H<sub>2</sub>O purge part of each ALD cycle reduced film thickness by ~7% and ~25%, and increased  $n$  by ~2% and ~6%, respectively, across a 150 mm Si wafer as compared to a control without MWs (Fig. 1). Preliminary electrical measurements on MOS devices indicate an associated reduction in low field leakage. Additional electrical and analytical data will be presented, including MWE-ALD deposition temperatures.

1. Conley, Jr. *et al.*, Appl. Phys. Lett. 84, 1913 (2004).
2. Conley, Jr. *et al.*, MRS Proc. Vol. 811, 5 (2004).
3. Conley, Jr., *et al.*, in *Physics and Technology of High-k Gate Dielectrics II*, ECS Proc. vol. 2003-22.
4. Clark *et al.*, ECS Trans. 41(2), 79 (2011).
5. Henke *et al.*, ECS J. Sol. Sta. Sci. Tech. 4(7), 277 (2015)
6. Miikkulainen *et al.*, ECS Trans. 80(3), 49 (2017).
7. Chalker *et al.*, ECS Trans. 69, 139 (2015).
8. Holden *et al.* J. Vac. Sci. Technol. A. 40, 040401 (2022).
9. No *et al.*, J. ECS 153, F87 (2006).
10. Österlund *et al.* J. Vac. Sci. Tech. A 39, 032403 (2021).
11. Ueda *et al.*, Appl. Surf. Sci. 554, 149656 (2021).
12. Liu and Chang. J. Chem. Phys. 116, (2002).
13. Becher *et al.*, Adv. Eng. Mater. 2300677 (2023).

## Atomic Scale Processing Mini-Symposium

### Room 116 - Session AP2+EM+PS+TF-WeM

#### New Advances in Atomic Layer Deposition

**Moderators:** Ashley Bielinski, Argonne National Laboratory, USA, John F. Conley, Jr., Oregon State University

**11:15am AP2+EM+PS+TF-WeM-14 Direct Atomic Layer Processing (Dalp™): Revolutionizing Precision Coatings for Emerging Device Technologies, S. Santucci, M. Akbari, B. Borie, Mira Baraket, I. Kundrata, M. Plakhotnyuk, ATLANT 3D Nanosystems, Denmark**

As the microelectronics sector advances towards further miniaturization, precision in thin film deposition becomes crucial. Traditional Atomic Layer Deposition (ALD) techniques, vital for semiconductor manufacturing, often require extensive surface preparation, limiting throughput. ATLANT 3D's  $\mu$ DALP™ technology adapts ALD using microreactor technology for localized thin film deposition with accuracy down to a few hundred microns, maintaining all conventional ALD benefits. This approach uses micronozzles for precise delivery of precursors, allowing rapid film formation on targeted substrate areas under atmospheric conditions. The  $\mu$ DALP™ achieves a vertical resolution of 0.2 nm, offering exceptional precision.

This technology enhances conventional ALD's capabilities in selective patterning for microfluidic channels, optical gratings, and nanostructured surfaces, improving its use in next-generation device fabrication. This presentation will discuss how  $\mu$ DALP™ retains ALD's core advantages while enhancing scalability, processing speed, and cost-efficiency. We will highlight the transformative impact of  $\mu$ DALP™ on thin-film manufacturing across optics, photonics, MEMS, and advanced electronics, underscoring its potential to propel future innovations in energy storage and conversion, quantum computing, and advanced packaging solutions.

**Keywords:** Atomic Layer Deposition,  $\mu$ DALP™, Nanotechnology, Thin Film, Microelectronics.

Fig. 1. (a) Top view of aligned Si trenches (aligned horizontally) coated with a perpendicular line of TiO<sub>2</sub> (low magnification SEM). (b) Microfluidic precursor delivery concept: Schematic view of the delivery nozzle in frontal view (top) and in cross-section (lower panel).

#### References

- (1) Parsons, G. N.; Clark, R. D., 2020, 32(12), 4920–4953.
- (3) Kundrata, I.; Barr, M. K. S.; Tymeck, S.; Döhler, D.; Hudec, B.; Brüner, P.; Vanko, G.; Precner, M.; Yokosawa, T.; Spiecker, E., Small Methods 2022, 6(5), 2101546.

**11:30am AP2+EM+PS+TF-WeM-15 Electrical and Optical Properties of Macroscopic Nanocomposites Fabricated by ALD Infiltration and Pressure-Assisted Sintering of Nanoparticle Compacts, Benjamin Greenberg, K. Anderson, A. Jacobs, U.S. Naval Research Laboratory; A. Cendejas, American Society for Engineering Education; E. Patterson, J. Freitas, J. Wollmershauser, B. Feigelson, U.S. Naval Research Laboratory**

Over the past 20+ years, a wide variety of nanocomposite thin films with unique property combinations have been produced by atomic layer deposition (ALD) infiltration of nanoparticle (NP) films. Examples include electrochromic WO<sub>3-x</sub> NP films with photochemical stability enhanced by Ta<sub>2</sub>O<sub>5</sub> ALD<sup>1</sup> and superhydrophilic and antireflective TiO<sub>2</sub>/SiO<sub>2</sub> NP films with elastic modulus and hardness enhanced by Al<sub>2</sub>O<sub>3</sub> ALD.<sup>2</sup> Applications of such nanocomposite films, however, are limited by their small thickness (typically a few  $\mu$ m or thinner), reliance on substrates, and/or residual porosity that can remain after ALD infiltration.

In this work, we explore fabrication of macroscopic, freestanding, dense nanocomposites—pucks with ~1 mm thickness, ~10 mm diameter, and solid volume fraction that can exceed 99%—via ALD infiltration of NP compacts followed by pressure-assisted sintering. For a prototype, we use monodisperse 100 nm SiO<sub>2</sub> NPs and an ALD coating of Al-doped ZnO to form electrically conductive ceramic nanocomposites with electrical and optical properties dependent on the coating thickness. Infiltration of the ultra-high-aspect-ratio (>10,000) SiO<sub>2</sub> NP compacts with ZnO:Al is accomplished via a recently developed cyclical-temperature ALD process.<sup>3</sup> The ZnO:Al-coated SiO<sub>2</sub> compacts are then densified via environmentally controlled pressure-assisted sintering (EC-PAS), wherein NPs are cleaned and kept in an inert atmosphere to maintain high surface energy, which enables low-temperature densification with minimal grain growth.<sup>4</sup> An EC-PAS process with a maximum pressure of ~2 GPa and a maximum temperature of 450 °C yields dense SiO<sub>2</sub>/ZnO:Al nanocomposites that contain nanocrystalline ZnO:Al networks and exhibit low electrical resistivity,  $\rho$ . At nominal ZnO:Al coating thicknesses,  $t$ , of ~3 nm and ~6 nm,  $\rho$  is on the order of 1 and 0.1  $\Omega$ -cm, respectively, at 300 K. Moreover, at  $t \approx 6$  nm, the Hall mobility approaches 1 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> at 300 K, and  $\rho$  increases by less than a factor of 3 upon cooling to 10 K, suggesting proximity to the metallic/band-like charge transport regime. Interestingly, the nanocomposites are blue in color with transparency and hue apparently dependent on  $t$ . Characterization techniques employed in our investigation into these electrical and optical properties include X-ray diffractometry, scanning electron microscopy, Hall and Seebeck effect measurements, absorption/transmission/reflection spectroscopy, and photoluminescence spectroscopy and imaging.

1. Y. Wang *et al.*, Chem. Mater. 28, 7198 (2016)
2. M. I. Dafinone *et al.*, ACS Nano 5, 5078 (2011)
3. B. L. Greenberg *et al.*, J. Vac. Sci. Technol. A 42, 012402 (2024)
4. H. Ryou *et al.*, ACS Nano 12, 3083 (2018)

**11:45am AP2+EM+PS+TF-WeM-16 Tunable Growth of Layered Double Hydroxide Nanosheets through Hydrothermal Conversion of ALD Seed Layers, Daniel Delgado Cornejo, A. Ortiz-Ortiz, K. Fuelling, University of Michigan, Ann Arbor; A. Bielinski, Argonne National Laboratory, USA; T. Ma, N. Dasgupta, University of Michigan, Ann Arbor**

Nano-architected materials have seen a rise in recent years and have produced advancements in a variety of fields including biomedicine, energy storage, and catalysis. As such, there is great motivation to develop novel synthesis and processing methods designed to improve the degree of fine control over the material's geometric parameters. In this study, we explore a method known as surface-directed assembly which makes use of the synergy between atomic layer deposition (ALD) and hydrothermal synthesis to grow layered-double hydroxide (LDH) nanosheets. The formation of the LDH product stems from the interaction between the deposited ALD Al<sub>2</sub>O<sub>3</sub> film and an aqueous zinc solution. Unlike other reported seeded hydrothermal syntheses, which rely on epitaxial growth from a seed layer, this interaction results in the consumption and conversion of the initial ALD film into the LDH product, where aluminum from the ALD film serves as a limiting reagent in the kinetic processes of nucleation and growth. Geometric parameters such as the nanosheet inter-spacing and length can be tuned by varying the thickness of the ALD film with sub-nanometer precision. A non-linear trend in nanosheet length is observed and characterized within three regimes: (I) depletion limited, (II) length independent, and (III) steric hindrance. In addition, we observe an inverse relationship between the nanosheet inter-spacing and the ALD film thickness. Finally, this process enables the formation of hierarchical nanostructured surfaces onto three-dimensional substrates including microposts, paper fibers, and porous ceramic supports. By leveraging the

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tunability and conformality of the ALD process, this work enables the programmable control of nano-architected material geometries for a variety of applications, including for energy and medical devices.

12:00pm **AP2+EM+PS+TF-WeM-17 Passivation Strategies for Far-Ultraviolet Al Mirrors Using Plasma-Based AlF<sub>3</sub> Processing**, *Maria Gabriela Sales, D. Boris*, U.S. Naval Research Laboratory; *L. Rodriguez de Marcos*, NASA Goddard Space Flight Center; *J. Hart, A. Lang, B. Albright, T. Kessler*, U.S. Naval Research Laboratory; *E. Wollack, M. Quijada*, NASA Goddard Space Flight Center; *S. Walton, V. Wheeler*, U.S. Naval Research Laboratory  
Far-ultraviolet (FUV) astronomy ( $\lambda = 100\text{-}200\text{ nm}$ ) relies on efficient Al mirrors because Al has a very high theoretical reflectance in this region. However, since Al readily oxidizes in air, the strongly absorbing native oxide layer appreciably degrades its FUV performance. A novel surface passivation technique for Al mirrors was previously demonstrated using an electron beam (e-beam) generated SF<sub>6</sub>/Ar plasma, which proceeds via a combined etching of the native oxide and simultaneous fluorination of the Al surface [1].

In our present work, this novel e-beam plasma technique is integrated into a plasma-enhanced atomic layer deposition (PEALD) system. We use a Veeco Fiji G2 reactor, equipped with substrate biasing, that has been uniquely modified to include an on-axis e-beam generated plasma source. Trimethylaluminum (TMA) and SF<sub>6</sub>/Ar plasma, produced with an inductively coupled plasma (ICP) source, were used as our precursor and reactant for the ALD AlF<sub>3</sub> process. Optimization of the ALD parameters was performed, and our best ALD AlF<sub>3</sub> films (F/Al  $\approx 3$ ,  $\sim 1\%$  oxygen content, and roughness  $< 1\text{ nm}$ ) were attained using 100 W ICP power and total plasma gas flows  $> 30\text{ sccm}$ . Our ALD AlF<sub>3</sub> films provide improved FUV reflectivity compared to oxidized bare Al, however, these optical properties are still limited by Al oxide at the AlF<sub>3</sub>/Al interface. To overcome this, we utilize our in-situ e-beam plasma, produced in a gas mixture of SF<sub>6</sub>/Ar, to minimize the native oxide layer prior to ALD.

In this talk, we discuss the processing parameters of the in-situ e-beam plasma (SF<sub>6</sub>/Ar ratio and flow, sample bias) and how they affect the AlF<sub>3</sub> growth rate, film/interface chemistry, and surface roughness. These material properties are related to optical performance, which compares favorably to state-of-the-art coatings ( $\approx 90\%$  at 121 nm). We then discuss hybrid AlF<sub>3</sub> films, in which the growth is initiated by e-beam plasma, and then continued using an optimized ALD AlF<sub>3</sub> recipe. For the initial step, pre-treatments using the in-situ e-beam plasma and the previously developed ex-situ e-beam plasma [1] are compared. We show that both in-situ and ex-situ hybrid techniques significantly reduce the interfacial oxygen compared to ALD AlF<sub>3</sub> alone (no pre-treatment), which enhances the FUV reflectivity. This work highlights the importance of the interface quality of passivated Al mirrors on their optical performance in the FUV range.

This work is supported by NASA Astrophysical Research and Analysis (APRA) grant 20-APRA20-0093/ N0017322GTC0044 and is partially supported by the NRL Base program through the Office of Naval Research.

[1] Rodriguez de Marcos, et al., Opt. Mater. Express 11, 740-756 (2021)

## Electronic Materials and Photonics

### Room 114 - Session EM+AIML+AP+QS+TF-WeM

#### Ferroelectrics and Memory Devices

**Moderators:** *Samantha Jaszewski*, Sandia National Labs, *Erin Cleveland*, Laboratory of Physical Sciences

8:00am **EM+AIML+AP+QS+TF-WeM-1 A Scalable Ferroelectric Non-Volatile Memory Operating at High Temperature**, *Dhiren Pradhan*, Department of Electrical and Systems Engineering, University of Pennsylvania; *D. Moore*, 2Materials and Manufacturing Directorate, Air Force Research Laboratory, Wright-Patterson AFB; *G. Kim*, Department of Engineering Chemistry, Chungbuk National University, Cheongju, Republic of Korea; *Y. He*, Department of Electrical and Systems Engineering, University of Pennsylvania; *P. Musavigharavi*, Department of Materials Science and Engineering, University of Central Florida; *K. Kim, N. Sharma, Z. Han, X. Du*, Department of Electrical and Systems Engineering, University of Pennsylvania; *V. Puli*, Materials and Manufacturing Directorate, Air Force Research Laboratory, Wright-Patterson AFB; *E. Stach*, Department of Materials Science and Engineering, University of Pennsylvania; *W. Kennedy, N. Glavin*, Materials and Manufacturing Directorate, Air Force Research Laboratory, Wright-Patterson AFB; *R. Olsson III, D. Jariwala*, Department of Electrical and Systems Engineering, University of Pennsylvania

Non-volatile memory (NVM) devices that reliably operate at temperatures above 300 °C are currently non-existent and remain a critically unmet challenge in the development of high-temperature (T) resilient electronics. There are numerous emerging harsh environment applications including aerospace, space exploration, oil and gas exploration, nuclear plants, mining and others that require complex, in-situ computing and sensing capabilities, for which high temperature NVM is critical. Current Silicon (Si)-based micro(nano)electronics, utilizing complementary metal oxide semiconductor (CMOS) technology, encounter reliability challenges above 200 °C and cannot retain their functional properties at high temperatures. Ferroelectric Al<sub>x</sub>Sc<sub>1-x</sub>N exhibits strong potential for utilization in NVM devices operating at very high temperatures ( $> 500\text{ °C}$ ) given its stable and high remnant polarization ( $P_R$ ) above  $100\mu\text{C}/\text{cm}^2$  with demonstrated ferroelectric transition temperature ( $T_C$ )  $> 1000\text{ °C}$ . Here, we demonstrate an Al<sub>0.68</sub>Sc<sub>0.32</sub>N ferroelectric diode based NVM device that can reliably operate with clear ferroelectric switching up to 600 °C with distinguishable On and Off states. The coercive field ( $E_C$ ) from the Triangle Wave I-V measurements is found to be  $-5.84 (E_C)$  and  $+5.98 (E_C)$  ( $\pm 0.1$ ) MV/cm at room temperature (RT) and found to decrease with increasing temperature up to 600 °C. The devices exhibit high remnant polarizations ( $> 100\mu\text{C}/\text{cm}^2$ ) which are stable at high temperatures. At 600 °C, our devices show 1 million read cycles with On-Off ratio above 1 for  $> 60$  hours. Finally, the operating voltages of our AlScN ferrodiodes are  $< 15\text{ V}$  at 600 °C which is compatible with Silicon Carbide (SiC) based high temperature logic technology, thereby making our demonstration a major step towards commercialization of NVM integrated high-T computers. NVM characteristics of engineered ferrodiodes with higher On-Off ratios at  $> 600\text{ °C}$  will also be presented in the meeting.

<sup>a</sup>Dhiren K. Pradhan and David C. Moore contributed equally to this work.

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8:15am **EM+AIML+AP+QS+TF-WeM-2 Oxygen Diffusion Coefficients in Ferroelectric Hafnium Zirconium Oxide Thin Films**, *Jon Ihlefeld, L. Shvilberg*, University of Virginia; *C. Zhou*, North Carolina State University

Just over a decade ago, ferroelectricity – the presence of a permanent reorientable dipole – was reported in doped hafnium oxide thin films. This report generated a great deal of excitement as the inherent silicon compatibility of HfO<sub>2</sub>, coupled with the extreme thinness of the films that exhibited the ferroelectric response promised to overcome a number of technological hurdles limiting utilization of ferroelectrics in microelectronics. While the material is moving toward mass production, there are lingering issues of insufficient endurance and limited retention. These issues are commonly attributed to oxygen point defects, including the drift of these defects in poled devices. As such, knowledge of oxygen transport in the ferroelectric phase is vital toward overcoming the current shortcomings. In this presentation, we will show the results of experiments using <sup>18</sup>O tracers to evaluate the diffusion coefficient of oxygen in the ferroelectric phase. Hafnium zirconium oxide films containing <sup>16</sup>O were prepared via plasma-enhanced atomic layer deposition followed by post-metallization annealing to form the ferroelectric phase. Following removal of the metal layer, an <sup>18</sup>O-containing hafnium zirconium oxide film was

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deposited via thermal atomic layer deposition with  $^{18}\text{O}$  provided from a  $\text{H}_2^{18}\text{O}$  source. Tracer anneals were then performed and the  $^{18}\text{O}$  position evaluated with secondary ion mass spectrometry. The results will show that the oxygen diffusion coefficients in the ferroelectric phase are extremely low, with extrapolated room temperature values of only  $10^{-26}$   $\text{cm}^2/\text{sec}$  derived. The activation energy for oxygen diffusion was calculated to be 1 eV, which is intermediate the values calculated for the equilibrium monoclinic phase and amorphous films. These results indicate that oxygen vacancies may be relatively immobile in ferroelectric hafnia devices and that other charged defects may be the primary source of degradation.

9:00am **EM+AIDL+AP+QS+TF-WeM-5 Iridium Etching: Exploring Reactive Ion Etching Parameters for Efficient Electrode Fabrication in Ferroelectric Memory**, Yanan Li, P. Bezdard, S. Kundu, F. Lazzarino, X. Piao, Y. Canvel, IMEC Belgium

Non-volatile Ferroelectric lead zirconium titanate (PZT) are interesting candidates for future memory applications but the fatigue resistance of the electrode material from the capacitors is a challenge. Iridium (Ir) is being investigated as electrode material for its superior characteristic. Thus, a patterning process must be developed. Due to the low volatility of the etch products, etching Ir is typically performed by ion beam etching (IBE). The low-throughput, relative scarcity of IBE chambers in the industry, as well as the limited tunability of the sputtering process are motivations for the development of a plasma-based etching approach.

In this work, we conducted experiments with TiN as a hard mask, following the process flow shown in Figure 1. Preliminary data indicates that Ir can be etched using both fluorine-based and chlorine-based gases. We identify and highlight the primary parameters affecting the Ir etch rate in the RIE process, focusing on gas flow rates, power settings, pressure, and substrate temperature. We also compare the relative contributions of physical and chemical reactions to the etch rate of Ir.

XSEM pictures for those experiments are shown in figures 2 and 3. It is observed that selectivity with a TiN hard-mask is a challenge when using these chemistries. Sidewall residues have also been observed in conditions where ion sputtering is dominant. Therefore, optimization of the etch processes based upon an understanding of the etch mechanisms in place is necessary.

9:15am **EM+AIDL+AP+QS+TF-WeM-6 Investigations in Current Transport Mechanisms of Multi-Resistance State Hafnia Zirconia Ferroelectric Tunnel Junctions**, Troy Tharpe, Sandia National Laboratories; M. Lenox, University of Virginia; S. Jaszewski, G. Esteves, Sandia National Laboratories; J. Ihlefeld, University of Virginia; M. Henry, Sandia National Laboratories

Since the discovery of ferroelectricity in doped hafnia ( $\text{HfO}_2$ ) and alloyed hafnia zirconia thin films ( $\text{Hf,ZrO}_2$ ) over a decade ago, fluorite-structure binary oxides have garnered great interest for use within ferroelectric memory devices to realize compute-in-memory (CIM) and neuromorphic applications. With conformal atomic layer deposition (ALD) techniques, process temperatures below  $400^\circ\text{C}$ , coercive fields close to  $1\text{ MV/cm}$ , and ferroelectricity down to  $\sim 1\text{ nm}$ , hafnia thin films are ideal candidates for back-end-of-line (BEOL) integration with complementary metal oxide semiconductor (CMOS) circuits. Leveraging these qualities, recent research has extensively focused on charge-based hafnia devices, such as ferroelectric random access memory (FeRAM) and ferroelectric tunnel junctions (FTJs). FTJs are realized by sandwiching a 4-7nm ferroelectric between electrodes to form a metal-ferroelectric-metal (MFM) structure with a voltage-controlled resistance modulated by polarization. Thinner than FeRAM and able to generate multistate resistances, FTJs are poised to enable energy efficient CIM devices and artificial intelligence (AI) hardware accelerators with improved performance and small form factor.

In this work, we study FTJs with 7 nm thick  $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$  deposited by plasma enhanced ALD, and asymmetric 20 nm niobium (Nb) / 115 nm niobium nitride (NbN) electrodes deposited by magnetron and reactive sputter, respectively. Film ferroelectricity is stabilized by subsequent anneal at  $565^\circ\text{C}$  for 90s in argon ambient. Fig. 1 (a) depicts an optical image of fabricated HZO FTJs while Fig. 1 (b) illustrates a cross section of device layers. Current density vs voltage (J-V) sweeps are taken at 294, 323, 348, 373, and 398 K for HZO FTJs with diameters varying from  $74\ \mu\text{m}$  to  $117\ \mu\text{m}$ . Fig. 2 (a) shows these J-V sweeps for a  $100\ \mu\text{m}$  diameter device, after application of 10 wakeup cycles. Fig. 2 (b) shows high resistance state (HRS) and low resistance state (LRS) trends across temperature for this same device at 0.2V and 0.3V. Fig. 3 (a, b) shows average and outlier resistance ratio (RR) temperature dependence for 4 devices at 0.2 V and 0.3V, respectively. Fig. 3 (c) depicts pulsed hysteresis curves for a  $99\ \mu\text{m}$  diameter device at 294 K and 398 K. Device resistance is read at 0.2V and a pulse width of 100ms,

following a write pulse progressing from 1.5V to 1.3V and back with 100mV step and 100ms pulse width. The nonlinear HRS, LRS and RR temperature trends indicate a complex conduction system within HZO FTJs, highlighting the need for continued investigation of current transport mechanics for the realization of ferroelectric CIM devices and multistate AI accelerators.

9:30am **EM+AIDL+AP+QS+TF-WeM-7 Correlation between Elastic Modulus and Biaxial Stress in Hafnium Zirconium Oxide (HZO) Thin Films**, Megan Lenox, University of Virginia; S. Jaszewski, Sandia National Laboratories; S. Fields, Naval Research Laboratory; A. Salanova, M. Islam, M. Hoque, University of Virginia; J. Maria, Penn State University; P. Hopkins, J. Ihlefeld, University of Virginia

The discovery of ferroelectricity in hafnium oxide based thin films has catalyzed significant research focused on understanding the ferroelectric property origins when fabricated in conventional metal-ferroelectric-metal geometries. Studies have revealed that electrode material selection impacts oxygen vacancies, interfacial layers, and biaxial stress, all noted responsible ferroelectric mechanisms. The coefficient of thermal expansion (CTE) incongruity between the hafnia and the electrode material induces an in-plane tensile stress following post-metallization annealing. However, recent work has shown that while the electrode material CTE does have an effect, the overall strain resulting from the device is primarily from the CTE of the silicon substrate and densification of the hafnia film during crystallization. This notwithstanding, comparisons between electrode materials have shown significant differences in ferroelectric remanent polarization ( $P_r$ ) behavior. This work describes these polarization differences through the lens of the elastic modulus of the electrode material. TaN/HZO/TaN/M devices, where M is platinum, TaN, iridium, tungsten, and ruthenium, were fabricated using plasma enhanced atomic layer deposition and sputtering for the hafnia and metal layers, respectively. Wafer flexure measurements done using stylus profilometry revealed each metal electrode material was compressive as deposited. Two-dimensional X-ray diffraction, utilized to derive the  $\sin^2(\psi)$  in-plane biaxial stress in the HZO, revealed a strong correlation between stress and electrode elastic modulus (E). Further, Polarization-electric field ( $P(E)$ ) measurements at  $2.5\text{ MV cm}^{-1}$  field also showed dependence of  $P_r$  on measured E. Conversely, no correlation exists between the electrode CTE and  $P_r$  or biaxial stress, respectively. Increasing modulus results in a greater resistance to deformation of the electrode, which when deposited prior to annealing the HZO to crystallize from the amorphous state, restricts the out-of-plane expansion of the HZO, promoting the stabilization of the ferroelectric orthorhombic phase, in a phenomenon known as the "capping effect". This work further promotes the acceleration integration of HZO into MFM devices, such as a non-volatile memory devices.

9:45am **EM+AIDL+AP+QS+TF-WeM-8 Ferroelectric Behavior of  $\epsilon\text{-WO}_3$** , Mohammad Mahafuzur Rahaman, A. Annerino, J. Shell, P. Gouma, The Ohio State University

Designing novel ferroelectric polymorphs having fast and low energy dipole switching responses is crucial for developing next generation's neuromorphic devices. Reported here a unique binary ferroelectric polymorph called  $\epsilon\text{-WO}_3$  and its dipole response to electro-optical stimuli, contributed from the stabilization of  $\epsilon$ -phase nanoparticles of  $\sim 20\text{ nm}$  grains at RT, previously was at  $-43^\circ\text{C}$  in bulk, by our group using FSP. The epsilon phase of the material is confirmed from XRD and Raman analysis. The nano-domains of ferroelectric  $\epsilon\text{-WO}_3$  shows switching behavior within few KV/cm electric field. The ferroelectric nanodomains interact with light and shows blue coloration under electro-optical stimuli. The response of these nanodomains with visible light and its switching behavior with electric field is studied via C vs V measurement. Furthermore, the origin of the observed "ferro-chromic effect", the unique, rapid and reversible coloration of the  $\epsilon\text{-WO}_3$  thin films upon application of a voltage in the absence of an electrolyte has been deduced from X-ray Photoelectron Spectroscopy. An important finding for all solid-state single layer ubiquitous displays, energy-saving windows and next generation's non-volatile memory device for neuromorphic computation.

11:00am **EM+AIDL+AP+QS+TF-WeM-13 Innovations in DARPA's Optimum Processing Technology Inside Memory Arrays (OPTIMA) Program**, Todd Bauer, DARPA

Fast, compact, and power-efficient compute-in-memory (CIM) accelerators can move machine learning from data centers to edge compute devices, enabling training and inference to be done where the training data is collected. However, conventional accelerators that use vonNeumann architecture have poor area and computational power efficiency and

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long execution latency. CIM architectures with Multiply Accumulate Macros (MAMs) can address the power and performance limitations of approaches that use von Neumann hardware architectures. To date these MAM implementations have been hindered by the large physical size of memory elements and the high-power consumption of supporting circuitry. The Defense Advanced Research Program Agency's Optimum Processing Technology Inside Memory Arrays (OPTIMA) program seeks to develop area- and power-efficient high-performance MAMs within innovative signal processing circuits. The key technical challenges that performers are addressing include 1) developing area-efficient, multi-bit memory elements (i.e. 8 bits of storage in a 1T-1C structure) that can be incorporated into compact multiply compute elements (MCEs) and 2) achieving compact, scalable, and power-efficient MAM circuits. This presentation will provide an overview of the OPTIMA program goals and approaches to achieving those goals.

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11:30am **EM+AIML+AP+QS+TF-WeM-15 A Transition Toward Solid-State in TiO<sub>2</sub> Protonic ECRAM**, *John Hoerauf*, University of Maryland, College Park; *M. Schroeder*, Army Research Laboratory; *D. Stewart*, *G. Rubloff*, University of Maryland, College Park

AI and inference learning energy demands are on pace to surpass global energy production<sup>1</sup>, but analog in-memory computing hardware can reduce the energy required by up to six orders of magnitude<sup>2</sup>. Electrochemical RAM (ECRAM) is a new and promising transistor technology to realize physical neuromorphic analog in-memory computing circuits, achieved on the device level by modifying a thin-film battery stack to measure the impedance of a selected electrode. The impedance is controlled by changing the state of charge of the battery, electrochemically doping the selected electrode with the electrochemically active species. ECRAM that utilizes protons as the electrochemically active species is compatible with existing CMOS devices, has faster programming speed and increased device durability compared to more established Lithium ion ECRAM. As a less well studied system, it is helpful to understand the insertion of protons in and out of the electrode of interest using a more traditional liquid cell before advancing to a solid-state system. In this presentation, the liquid cell electrochemical characteristics and degradation mechanisms in anatase TiO<sub>2</sub> are discussed with and without a capping Nafion film. It is observed that the anatase TiO<sub>2</sub> electrode's typically quick degradation is suppressed by adding a spin-cast Nafion film, increasing cyclability in an aqueous acetate buffer solution by >10x cycles and altering the H<sup>+</sup> insertion kinetics. Subsequently, TiO<sub>2</sub> is used in an all-solid-state three electrode transistor by splitting the bottom current collector into a source-drain configuration and using PdH<sub>2</sub> as the counter electrode and H<sup>+</sup> reservoir. Results toward novel solid state anatase TiO<sub>2</sub> based protonic ECRAM are discussed with a focus on device state modulation by electrochemical doping.

[1] B. Bailey, "AI Power Consumption Exploding," Semiconductor Engineering. Accessed: May 09, 2024. [Online]. Available: <https://semiengineering.com/ai-power-consumption-exploding/>

[2] E. J. Fuller et al., "Li-Ion Synaptic Transistor for Low Power Analog Computing," *Advanced Materials*, vol. 29, no. 4, p. 1604310, 2017

11:45am **EM+AIML+AP+QS+TF-WeM-16 Effects of Gamma Radiation on the Structural and Ferroelectric Properties of Hafnium Zirconium Oxide Capacitors**, *Samantha Jaszewski*, Sandia National Laboratories; *M. Lenox*, *J. Ihlefeld*, University of Virginia; *M. Henry*, Sandia National Laboratories

Ferroelectric hafnium oxide (HfO<sub>2</sub>) presents opportunities for technological developments in microelectronics, such as scaling of ferroelectric random-access memory (FeRAM) and new devices such as ferroelectric field-effect transistors (FeFETs) and ferroelectric tunnel junctions (FTJs), that were not previously possible with conventional ferroelectrics. This is due to its compatibility with silicon and ability to exhibit a ferroelectric response in films as thin as 1 nm. Understanding the interaction between radiation and HfO<sub>2</sub>-based ferroelectrics is necessary before this material can be utilized in devices facing radiation-hostile environments. In this work, the effects of varying doses of gamma radiation (1 to 8 Mrad) on the structural and electrical properties of metal-ferroelectric-metal capacitors fabricated with 17 nm thick hafnium zirconium oxide (HZO) layers is investigated. Additionally different electrode materials, titanium nitride and tungsten, will be compared. Polarization-electric field, capacitance-voltage, and leakage current measurements were made after electric field cycling with voltages ranging from 2.6 to 4 V. It will be shown that the devices experience decreased endurance and a shift in the coercive voltage that scales with the applied gamma dose and depends on the electrode

material. Synchrotron nano-Fourier transform infrared spectroscopy measurements demonstrated that no significant phase changes occur after radiation in these films. This work advances the understanding of the interaction between radiation and HfO<sub>2</sub>-based ferroelectrics in order to probe the fundamental limits of radiation tolerance in this material.

12:00pm **EM+AIML+AP+QS+TF-WeM-17 Reconfigurable Ferroelectric Field-Effect Transistor Arrays from SWCNTs**, *Dongjoon Rhee*, *K. Kim*, *S. Song*, University of Pennsylvania; *L. Peng*, Peking University, China; *J. Kang*, Sungkyunkwan University (SKKU), Republic of Korea; *R. Olsson III*, *D. Jariwala*, University of Pennsylvania

Ferroelectric field-effect transistor (FeFET) is a promising nonvolatile memory device due to its simple and compact device structure for high-density integration, fast switching speed, and non-destructive readout. Recent progress in FeFETs based on two-dimensional (2D) semiconductor channels and ferroelectric Al<sub>0.68</sub>Sc<sub>0.32</sub>N (AlScN) has enabled high-performance nonvolatile memory devices with remarkably high ON-state currents, large current ON/OFF ratio, and large memory windows. However, the wafer-scale synthesis of these 2D semiconductors typically demands growth temperatures exceeding 500 °C, rendering the synthesis process incompatible with back-end-of-line (BEOL) processing and necessitating a subsequent transfer step. Solution-based assembly of semiconducting single-walled carbon nanotube (SWCNT) has shown promise as a strategy to fabricate high-quality semiconducting channels at room temperature, but their integration with AlScN for FeFETs has not yet been achieved. In this work, we present a large array of FeFETs utilizing a dense monolayer film of highly aligned semiconducting SWCNTs and ferroelectric AlScN. Our SWCNT FeFETs can be engineered from *p*-type to ambipolar by changing the contact metals at the metal-semiconducting interface. The ambipolar FeFETs showed high electron and hole current densities, both exceeding 300 μA μm<sup>-1</sup>, along with stable memory retention over 10<sup>4</sup> s and endurance greater than 10<sup>4</sup> cycles. Our devices can also function as reconfigurable *p*- and *n*-FETs by switching the polarization direction of AlScN, potentially enabling multifunctional logic and memory applications at the circuit level.

## Electronic Materials and Photonics

### Room 114 - Session EM+AP+TF-WeA

#### CMOS and BEOL - Advances in Materials Integration and Devices

**Moderators:** Erica Douglas, Sandia National Laboratories, Cheng Gong, University of Maryland College Park

#### 2:15pm EM+AP+TF-WeA-1 All-Acoustic and Single-Chip Radio Frequency Signal Processing via Heterogeneous Integration of Semiconductors and Piezoelectric Materials, *Matt Eichenfeld*, University of Arizona **INVITED**

Radio frequency front-end signal processors are the workhorses of modern communications and sensing, providing the signal processing link between data and the radio waves that carry that data between transmitters and receivers. These front-end processors typically use a mix of piezoelectric acoustic microchips and semiconductor transistor microchips to achieve the many different functions they need to encode and decode information. Because of the very disparate materials used, these different chips are assembled at the system level into so-called multi-chip modules, and this system-level integration greatly increases the size of RF systems and degrades their performance. In this talk, I will describe how we have used heterogeneous integration of semiconductor materials with piezoelectric materials such as lithium niobate to create the first-ever comprehensive platform for radio-frequency signal processing with gigahertz frequency acoustic waves. This all-acoustic approach means that the entire front-end processor can be made on a single chip, paving the way towards wireless technologies with more than a 100x reduction in form-factor, as well as increased performance and lower power consumption. It is also a sandbox for studying and engineering the complex interactions between electrons and phonons in solid state materials that may lead to new discoveries and innovations in electronics, phononics, and thermal transport.

#### 2:45pm EM+AP+TF-WeA-3 Breaking the Quantum Conductance Barrier in CMOS Interconnect Design, *William Kaden*, University of Central Florida

Moore's law miniaturization has greatly amplified the importance of interconnect resistance as the limiting factor controlling computational power consumption and clock-speed limitations. The most recent inflection point occurred when cross-sectional wire dimensions miniaturized below the electron mean free path for charge transport within the wire. This has led to deleterious deviations from bulk resistivity scaling trends as uncontrolled surface scattering contributions have become increasingly non-negligible. Searches for suitable replacements to copper for bottom level interconnects have emerged as a direct consequence, with a figure of merit consisting of  $\lambda^* \rho_0$  emerging as a primary screening criteria used to find materials best balancing bulk and surface contributions to wire resistivity within this size regime. With decreasing wire cross-sections has also come decreasing grain size, such that grain-boundary scattering also accounts for a significant fraction of the resistivity size effect trends observed in nanowire test-structures. Despite these challenges introduced by miniaturization, further miniaturization of bottom layer interconnect lengths now has the potential to beneficially reduce wire resistance via a fundamental change in charge-transport enabling ballistic conduction to emerge as wire lengths also begin to decrease below electron mean free paths. For reference, bottom layer interconnects are now comparable in length to the room temperature mean free path of bulk copper (~40 nm). Nonetheless, current interconnects do not support quantum conduction due to several non-phononic scattering contributions associated with interactions with grain boundaries, wire surfaces, and defects, such that the effective electron mean free path observed in industrially fabricated nanowires is far less than that of the bulk metals from which they are composed. To successfully leverage the potential for quantum conductance at current interconnect dimensions, non-phononic contributions to resistivity must first be mitigated. Our group has aimed to achieve this through the creation of high-quality single-crystalline nanowire test-structures, for which we have established process-mediated phenomenological control over surface scattering specularly. To achieve this, our group has developed and characterized heteroepitaxial Ru(0001) thin-films deposited on Al<sub>2</sub>O<sub>3</sub>(0001) wafers, leveraged electron-beam lithography to subtractively pattern nanowire devices, and compared wire resistance observations at varied temperatures to establish ballistic contributions to conductance as a function of wire length and temperature.

#### 3:00pm EM+AP+TF-WeA-4 "Suboxide MBE" — A Route to p-Type and n-Type Semiconducting Oxides at BEOL Conditions, *Darrell Schlom*, Cornell University

In this talk\* I will describe a variant of molecular-beam epitaxy (MBE)—"suboxide MBE"—that makes it possible to deposit p-type and n-type semiconducting oxides with excellent structural perfection epitaxially at back end of line temperatures. In suboxide MBE the molecular beams consist of pre-oxidized elements (suboxides) that help navigate kinetic pathways. For example, supplying a molecular beam of indium suboxide (In<sub>2</sub>O) eliminates the rate limiting step of conventional MBE to the growth of In<sub>2</sub>O<sub>3</sub>—the oxidation of indium to its suboxide—and by skipping this step growth with excellent crystallinity, surface smoothness, and at a low growth temperature are achieved. Similarly, Sn<sup>2+</sup>-based p-type oxides that are challenging to deposit due to this delicate oxidation state may be deposited at BEOL conditions by utilizing suboxide MBE. In addition to extensive structural characterization, electrical characterization and working transistors will also be shown.

\*This work was performed in collaboration with coauthors from the groups of: S. Chae, K. Cho, S. Datta, F. Giustino, C. Gugeshev, G. Hautier, F.V.E. Hensling, D. Jena, I.M. Kankanamge, Z.K. Liu, D.A. Muller, H. Paik, X.Q. Pan, N.J. Podraza, Y.E. Suyolcu, P.A. van Aken, P. Vogt, M.D. Williams, H.G. Xing, and P.D. Ye

#### 3:15pm EM+AP+TF-WeA-5 Epitaxial Metastable Cubic CO(001)/MgO(001): Potential Interconnect Conductor, *Anshuman Thakral*, *D. Gall*, RPI

The phase composition of Co layers deposited by magnetron sputtering is studied as a function of processing gas (Ar or N<sub>2</sub>), temperature  $T_s = 100$ -600 °C, and substrate [Al<sub>2</sub>O<sub>3</sub>(0001), MgO(001) and SiO<sub>2</sub>/Si] in order to determine the energetics for thin film synthesis of metastable fcc cobalt which has been theoretically predicted to be the most conductive metal in the limit of narrow interconnect lines. Nitrogen gas facilitates the growth of the metastable cubic phase particularly at  $T_s > 200$  °C. Cubic MgO(001) substrates suppress nucleation of hcp Co grains, resulting in fcc Co even in an Ar atmosphere. The highest crystalline quality epitaxial fcc Co(001) layers are obtained with deposition on MgO(001) in 5.0 mTorr N<sub>2</sub> using  $T_s = 400$  °C during deposition, followed by vacuum annealing at 500 °C. The resistivity size effect in FCC Co is quantified with transport measurements at 295 and 77 K. Data fitting with the Fuchs-Sondheimer model of the measured resistivity  $\rho$  vs thickness  $d = 5 - 1000$  nm for single-crystal Co(001)/MgO(001) layers indicates an effective electron mean free path  $\lambda_{eff} = 27 \pm 2$  nm at 295 K and a room-temperature bulk resistivity  $\rho_0 = 6.4 \pm 0.3$   $\mu\Omega$ -cm. At 77 K, the reduced electron-phonon scattering yields a smaller  $\rho_0 = 1.3 \pm 0.1$   $\mu\Omega$ -cm and a larger  $\lambda_{eff} = 79 \pm 6$  nm. The resulting benchmark quantity  $\rho_0 \lambda_{eff} = 17.4 \times 10^{16}$  and  $10.2 \times 10^{16}$   $\Omega$ -m<sup>2</sup> at 293 and 77 K, respectively, is 4-6 times larger than the first-principles predictions. The measured  $\rho_0$  for fcc Co is identical to that of the stable hcp Co phase. However due to the high effective mean free path and resulting high  $\rho_0 \lambda_{eff}$  values, cubic Co does not outperform hcp Co for interconnect applications. The developed method for growth of epitaxial fcc Co(001) layers provides opportunities to study this metastable material for potential spintronic applications.

#### 3:30pm EM+AP+TF-WeA-6 Characteristics of Reconfigurable FETs Implemented on Bulk Silicon Using Reduced Pressure CVD, *S. Lee*, *S. Kim*, *J. Park*, *W. Lee*, *Dongwoo Suh*, Electronics and Telecommunications Research Institute, Republic of Korea

As semiconductor process technology advances, tremendous efforts have been made in device engineering to mitigate the issue of integration density. One of the representative and prospective solutions is the novel device of reconfigurable FET, single FET working either as n- or p-MOSFET according to the polarity of gate bias. Because reconfigurable FET stands in need of intrinsic source/drain and channel, it has been fabricated on expensive and size-limited SOI wafers. Furthermore, its application is restricted to special devices leaving contemporary CMOS technology irrelevant. In the present study we fabricated reconfigurable FETs on bulk silicon wafers using a lateral epitaxial growth technique unleashing its application potential.

Starting with 6-inch p-type (100) wafers covered with the oxide layer of 0.1  $\mu$ m, we etched out the oxide layer to form a small seed zone following the epitaxial growth of intrinsic silicon from it using reduced pressure CVD. Having scrutinized the grown epilayer with high resolution transmission electron microscopy, we ensured that its crystal quality was very good in spite of local stacking faults. After planarization of the grown epilayer with CMP, we made Schottky contacts of titanium silicide both on the surface footprint of source and drain to form reconfigurable FET. Our device

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consists of single control gate in the center of the channel and two polarity gates placed symmetrically around it.

Current-voltage properties are investigated at the drain voltage of 1 Volt for various polarity gate potential. We obtained clear reconfigurable characteristics of n-MOS under positive gate bias and p-MOS vice versa reaching at the maximum current of 0.1  $\mu\text{A}/\mu\text{m}$  for nMOS and 0.8  $\mu\text{A}/\mu\text{m}$  for p-MOS operation. Transfer characteristics show higher current in p-MOS operation on the contrary to conventional FET. This result is caused by the difference of Schottky barrier height of titanium silicide for n-type (0.61 Volts) and P-type (0.49 Volts). Current levels are small overall because spatial gaps between two adjacent polarity and control gates are inevitably formed during the fabrication process. Notwithstanding the gap issue, our device can reduce the load of device integration. In addition, the present device can be a strong candidate for the mitigation of power issue in IC chips when cutting-edge CMOS technology is applied appropriately.

*This work was supported by a National Research Foundation of Korea (NRF) grant funded by the Korean government (MSIT)(Ministry of Science and ICT, NRF-2019M3F3A1A02076911).*

**4:15pm EM+AP+TF-WeA-9 Forward Bias Annealing of Proton Radiation Damage in NiO/Ga<sub>2</sub>O<sub>3</sub> Rectifiers, Jian-Sian Li, C. Chiang, H. Wan, University of Florida, Gainesville; M. Rasel, A. Haque, Pennsylvania State University; J. Kim, Seoul National University, Republic of Korea; F. Ren, University of Florida; L. Chernyak, University of Central Florida; S. Pearton, University of Florida**

17 MeV proton irradiation at fluences from 3-7  $\times 10^{13}$   $\text{cm}^{-2}$  of vertical geometry NiO/ $\beta$ -Ga<sub>2</sub>O<sub>3</sub> heterojunction rectifiers produced carrier removal rates in the range 120-150  $\text{cm}^{-1}$  in the drift region. The forward current density decreased by up to 2 orders of magnitude for the highest fluence, while the reverse leakage current increased by a factor of  $\sim 20$ . Low-temperature annealing methods are of interest for mitigating radiation damage in such devices where thermal annealing is not feasible at the temperatures needed to remove defects. While thermal annealing has previously been shown to produce a limited recovery of the damage under these conditions, athermal annealing by minority carrier injection from NiO into the Ga<sub>2</sub>O<sub>3</sub> has not previously been attempted. Forward bias annealing produced an increase in forward current and a partial recovery of the proton-induced damage. Since the minority carrier diffusion length is 150-200 nm in proton irradiated Ga<sub>2</sub>O<sub>3</sub>, recombination-enhanced annealing of point defects cannot be the mechanism for this recovery, and we suggest that electron wind force annealing occurs.

**4:30pm EM+AP+TF-WeA-10 Studies of the Effects of Doping and Nanolamination on the Temperature Coefficient of Resistivity of Ru-TiO<sub>2</sub> Thin Films, S. Berriel, Gouri Syamala Rao Mullapudi, University of Central Florida; N. Rudawski, University of Florida; P. Banerjee, University of Central Florida**

High precision electronics require the use of materials with constant resistivity across a wide range of temperatures. The metric of change of resistivity with temperature is known as temperature coefficient of resistivity (TCR). Low TCR is highly desirable for applications such as wearable strain sensors, automobile electronics, and microelectronics. Materials of low TCR can be difficult to come by. However, metals exhibit positive TCR, and semiconductors and insulators exhibit negative TCR. Thus, a combination of metallic and semiconducting materials could be used to create a net low TCR.

Atomic layer deposition (ALD) is a method well-suited to the task of tuning thin film composition between metal and insulator. To this end, we have studied the effect of nanolaminated-structured vs doped films on TCR for a temperature range spanning from 80 K to 420 K. The compositions of the thin films have been finely controlled by combining Ru - a metal, and TiO<sub>x</sub> - an insulator, using a Veeco Fiji G2 ALD chamber. Two types of films were made: First, a series of nanolaminates of 30 nm total thickness were synthesized with 50/50 composition Ru/TiO<sub>x</sub> while varying thickness of individual layers. Second, a set of films were made by dosing small amounts of TiO<sub>x</sub> into a predominantly Ru film totaling 30 nm thickness. The thickness of the total film and individual layers were monitored using *in situ* spectroscopic ellipsometry. The films have been further investigated via temperature-dependent van der Pauw, XRD, and TEM measurements to determine a cross-over from metallic to insulating behavior thus, precisely targeting a composition that produces low TCR behavior.

**4:45pm EM+AP+TF-WeA-11 Dorothy M. and Earl S. Hoffman Scholarship Awardee Talk: Determination of Band Offsets at the Interfaces of NiO, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and ITO with AlN, Hsiao-Hsuan Wan<sup>1</sup>, J. Li, C. Chiang, X. Xia, D. Hays, University of Florida; N. Al-Mamun, A. Haque, Pennsylvania State University; F. Ren, S. Pearton, University of Florida**

The valence and conduction band offsets at the interfaces between NiO/AlN, SiO<sub>2</sub>/AlN, Al<sub>2</sub>O<sub>3</sub>/AlN and ITO/AlN heterointerfaces were determined via x-ray photoelectron spectroscopy using the standard Kraut technique. These represent systems which potentially would be used for p-n junctions, gate dielectrics and improved Ohmic contacts to AlN, respectively. The band alignments at NiO/AlN interfaces are nested, type I heterojunctions with conduction band offset of -0.38 eV and valence band offset of -1.89 eV. The SiO<sub>2</sub>/AlN interfaces are also nested gap, type I alignment with conduction and offset of 1.50 eV and valence band offset of 0.63 eV. The Al<sub>2</sub>O<sub>3</sub>/AlN interfaces are type-II (staggered) heterojunctions with conduction band offset -0.47 eV and valence band offset 0.6 eV. Finally, the ITO/AlN interfaces are type-II (staggered) heterojunctions with conduction band offsets of -2.73 eV and valence band offsets of 0.06 eV. The use of a thin layer of ITO between a metal and the AlN is a potential approach for reducing contact resistance on power electronic devices, while SiO<sub>2</sub> is an attractive candidate for surface passivation or gate dielectric formation on AlN. Given the band alignment of the Al<sub>2</sub>O<sub>3</sub>, it would only be useful as a passivation layer. Similarly, the use of NiO as a p-type layer to AlN does not have a favorable band alignment for efficient injection of holes into the AlN.

**5:00pm EM+AP+TF-WeA-12 Ferroelectric Al<sub>0.2</sub>Sc<sub>0.8</sub>N Diodes on NbN Electrodes Deposited on Sapphire Substrates, Giovanni Esteves, T. Tharpe, T. Young, D. Henry, Sandia National Laboratories**

The emergence of wurtzite ferroelectrics and their scaling below 50 nm has significantly broadened their applications in microelectronics, extending their utility into harsh environments. Ferroelectric aluminum scandium nitride (Al<sub>1-x</sub>Sc<sub>x</sub>N) exhibits a unique diode behavior due to its internal switchable polarization. Although AlScN is often accompanied by high coercive fields ( $E_c$ ) exceeding 3 MV/cm, in contrast to its fluorite ferroelectric counterparts which have  $E_c$  values below 1 MV/cm, this high  $E_c$  is advantageous for high-temperature microelectronic applications where  $E_c$  decreases with temperature. When scaling the thickness below 50 nm, challenges related to achieving high crystallographic texture and accurate device measurements become significant. To address these challenges, this study explores the use of NbN films deposited on sapphire substrates to template the AlScN. X-ray diffraction results reveal that a 24 nm AlScN film inherits its in-plane texture from the underlying NbN film deposited on sapphire. Ferroelectric capacitors were fabricated using 100 nm NbN films as both top and bottom electrodes, and current-voltage (IV) measurements were conducted across multiple capacitors. The ratio of the high resistance state (HRS) to the low resistance state (LRS) was studied as a function of drive voltage, demonstrating changes ranging from 2x to 500x, with some capacitors exhibiting changes well above 1000x. The response between the HRS and LRS is controlled via the partial switching of domains—regions of uniform polarization—within the AlScN film. The promising results of this study pave the way for future applications of AlScN in non-volatile memory devices capable of operating at high temperatures, as well as in analog computing systems. Additionally, continued research into the effects of extreme environments on the ferroelectric response of AlScN will further enhance its potential for robust and reliable performance in demanding conditions. These advancements could significantly impact the development of next-generation microelectronic devices, offering improved functionality.

**5:15pm EM+AP+TF-WeA-13 Optimizing Sputtering Parameters for Tantalum Oxide-Based Resistive Memory: A Design of Experiments Approach, Alireza Moazzeni, Wayne State University; S. Karakaya, A. Khan, G. Tutuncuoglu, Wayne state university**

**Abstract**This study optimizes sputtering parameters for Tantalum Oxide-based Resistive Random-Access Memory (TaO<sub>x</sub> RRAM, 1<x<2.5) using the Design of Experiments (DOE). By varying oxygen partial pressure (20% and 35%) and DC power (75 W and 250 W), we aim to control device performance metrics like forming voltage and power consumption. Response Surface Methodology (RSM) and Central Composite Design (CCD) were used, with 12 experimental settings and four center points, to explore parameter interactions. The goal is to improve the uniformity and reliability of TaO<sub>x</sub> RRAM fabrication for future high-performance memory systems.

<sup>1</sup> AVS National Student Awardee

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**Introduction** Tantalum Oxide-based RRAM is a promising non-volatile memory technology for neuromorphic computing, integrating memory and processing to reduce data transfer bottlenecks [1]. TaO<sub>x</sub> RRAM's endurance, thermal stability, and scalability make it suitable for various applications [2]. The material's properties can be tuned via thin-film synthesis, particularly by adjusting DC sputtering parameters, allowing control over oxygen vacancies [3, 4]. TaO<sub>x</sub> RRAM has achieved fast switching, low power consumption, and high endurance, positioning it as a key technology for future computing systems [5]. Despite these advantages, variability, particularly forming voltage, remains a challenge [6]. This is influenced by oxygen vacancy concentration, film thickness, and sputtering conditions [7, 8]. Controlling these factors can reduce device variability [9]. While previous studies looked at oxygen pressure and power independently, this study explores their combined effects on performance. Design of Experiments (DOE), specifically RSM and CCD, was used to optimize the sputtering process within limited operational ranges. CCD allowed efficient exploration of factor values, while RSM provided a framework for modeling multiple variables. The objective is to optimize sputtering parameters, develop a predictive model, and enhance performance metrics like forming voltage and power consumption. Oxygen pressure levels (20% and 35%) and power levels (75 W and 250 W) were chosen with significant separation to identify key trends. Interactions between parameters were also examined, with four center points included for validation, resulting in 12 experimental settings. Figure 1 and Table 1 illustrate the setup and design points.

By optimizing sputtering parameters and investigating their interactions, this study aims to reduce variability in TaO<sub>x</sub> RRAM devices and improve performance metrics, contributing to the scalable integration of this technology in next-generation computing systems.

## Electronic Materials and Photonics

### Room 114 - Session EM+2D+AP+QS+TF-ThM

#### Epitaxy: Advances in Materials Integration and Devices

Moderator: Somil Rathi, Arizona State University

8:00am **EM+2D+AP+QS+TF-ThM-1 Electronic and Photonic Integrated Devices Enabled by Local III-V on Si Heteroepitaxy**, M. Scherrer, IBM Research GmbH, Zurich Research Laboratory, Switzerland; K. Moselund, Paul Scherrer Institute, Switzerland; **Heinz Schmid**, IBM Research GmbH, Zurich Research Laboratory, Switzerland

Heterogeneous integration of electronic chipllets is one of the key performance drivers in today's HPC and consumer products. Similarly, a performance benefit can be envisioned by heterogeneous integration of preferred materials at the device level. Here we explore this bottom-up path and report on local growth of III-V compound semiconductors on silicon for electronic and photonic applications. For electronic applications the high charge carrier mobility in III-V materials is particularly interesting, while for optical devices, the direct bandgap and in-plane coupling to Si waveguides are key benefits. We will detail the epitaxial growth of III-Vs on Si by template-assisted selective epitaxy using MOCVD and highlight this method's uses by discussing selected device characteristics for field-effect transistors [1] and pin photodetectors directly integrated to Si waveguides [2]. The dense and precise co-placement of III-V gain material with Si allows for novel device designs, which will be illustrated by recent results on lasers based on hybrid III-V/Si photonic crystal cavity designs [3].

This research is supported by EU Grant 860095, 678567, 735008 and SNF grant 188173.

[1] C. Convertino et al. Nat. Electron. (2021) doi.org/10.1038/s41928-020-00531-3

[2] P. Wen et al. Nat. Comm. (2022) doi.org/10.1038/s41467-022-28502-6.

[3] M. Scherrer et al. ACS Photonics (2024) doi.org/10.1021/acsp Photonics.3c01372

8:15am **EM+2D+AP+QS+TF-ThM-2 In situ Graphene Barriers for Remote Epitaxy of SiC**, **Daniel Pennachio**, J. Hajzus, R. Myers-Ward, US Naval Research Laboratory

Remote epitaxy (RE) is a thin film growth technique where epitaxial alignment is directed by interactions with a substrate despite it being covered by a top layer of material.[1] This top layer must be inert and atomically thin for the underlying substrate's potential field to dominate the epitaxial alignment. Since the intermediate layer is inert, the epitaxial thin film is weakly bonded to the substrate and can be removed as a freestanding membrane and the substrate can be reused, without the damage associated with other transfer techniques such as controlled cleaving or ion implantation. Transferred 2D two-dimensional (2D) material, such as graphene, is commonly used for a layer, but the transfer can degrade the film and increase process complexity. To avoid this, we aim to grow in situ graphene in the same chemical vapor deposition (CVD) RE growth as SiC. RE SiC is advantageous since the high cost of SiC makes substrate reuse appealing and isolated SiC membranes are excellent for quantum photonics. Despite these benefits, SiC's high-temperature hydrogen-containing CVD environment can easily damage graphene, making RE difficult.

This study established growth windows for in situ graphene via propane-based hot wall CVD followed by subsequent SiC deposition. Growing at 1620 °C in 20 slm H<sub>2</sub> with 20 sccm propane flow produced predominantly monolayer (ML) graphene films on on-axis 6H-SiC(0001) substrates and 2-3 ML films on 4° off-axis 4H-SiC(0001) substrates with minimal defects found in Raman spectral maps. These films exhibited increased uniformity over graphene grown via Si sublimation from the SiC substrate, as determined by atomic force microscopy (AFM) and Raman spectral maps. This optimal graphene growth condition was used for subsequent RE attempts to study the effect of SiC growth temperature, precursor C/Si ratio, and growth rate on epilayer crystallinity and graphene barrier damage. Nomarski microscopy, scanning electron microscopy (SEM), and AFM found SiC grown at 1620°C with a C/Si ratio of 1.55 to have the smoothest surface morphology and fewest polytype inclusions. SiC crystalline quality appeared correlated to growth rate, with lower growth rates producing smoother films with fewer polytype inclusions. Single-crystalline, polytype-pure SiC epilayers was achieved on 4° off-axis CVD graphene/4H-SiC(0001). Cross-sectional transmission electron microscopy (TEM) of some growth

interfaces in this study exhibited non-uniform multilayer graphitic carbon, motivating further study of this growth system to improve boundary uniformity and SiC epilayer quality.

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

8:30am **EM+2D+AP+QS+TF-ThM-3 Basal Plane Dislocation Mitigation via Annealing and Growth Interrupts**, **Rachael Myers-Ward**, N. Mahadik, D. Scheiman, J. Hajzus, S. White, D. Pennachio, Naval Research Laboratory

Basal plane dislocations (BPD) in SiC are high-voltage bipolar device killers that source Shockley-type stacking faults in the presence of an electron-hole plasma [1]. Multiple research groups have been successful in mitigating their propagation from the substrate into the epitaxial layer [2-5]. While these are sufficient for typical SiC devices, for high pulsed power current density or high surge current capability applications, the injected carrier concentration is significant enough to expand converted BPDs. Here, we will report results from comparisons of H<sub>2</sub> etching to Ar annealing and the use of H<sub>2</sub> versus Ar during growth interrupts to prevent BPD expansion.

SiC epitaxial layers were grown using a CVD reactor on 4° off-axis substrates toward the [11-20] that are known to have BPDs. A H<sub>2</sub> etch or Ar anneal was performed before the buffer layer (BL) growth while a growth interrupt in H<sub>2</sub> or Ar was conducted prior to the intentionally low doped drift layer. Ultraviolet photoluminescence (UVPL) imaging was used to image the samples before and after UV stressing up to 13 kWcm<sup>-2</sup>.

The H<sub>2</sub> etch and H<sub>2</sub> growth interrupt prevented BPDs from expanding under UV stress of 13kWcm<sup>-2</sup> and it is believed that the H<sub>2</sub> treatment specifically inhibited this expansion. To confirm the role of H<sub>2</sub>, we performed a growth using the same conditions as the H<sub>2</sub> etch/interrupt, however, an Ar anneal was used instead of a H<sub>2</sub> etch and the growth interrupt was conducted in an Ar atmosphere instead of H<sub>2</sub>. The sample was UV stressed up to 1000 Wcm<sup>-2</sup> and it was found that four BPD expanded from the substrate into the epilayer. For comparison, a sample grown with a double H<sub>2</sub> etch (before the buffer layer growth and drift layer) and a sample grown with a H<sub>2</sub> etch plus H<sub>2</sub> growth interrupt did not produce faulting at the same power density. This indicates that H<sub>2</sub> influences BPD expansion. We will present detailed parametric results of samples grown with various etching/annealing, growth interrupts, anneal times, buffer layer thickness, gas flow rates and interrupt temperature, both in H<sub>2</sub> and Ar.

[1]J.P. Bergman, et. al., Mater. Sci. Forum Vol. 353-356, 299 (2001).

[2]N.A. Mahadik et al., Mater Sci Forum 858, 233 (2016).

[3]R. E. Stahlbush, et al., Appl. Phys. Lett. 94, 041916 (2009).

[4]M. Kato, et al., Sci. Rep., 12, 18790 (2022).

[5]N.A. Mahadik et. al., Appl. Phys. Lett., 100, 042102 (2012).

8:45am **EM+2D+AP+QS+TF-ThM-4 Shadow Mask Molecular Beam Epitaxy**, S. Mukherjee, R. Sitaram, X. Wang, University of Delaware; **Stephanie Law**, Pennsylvania State University

Shadow mask molecular beam epitaxy (SMMBE) is a form of selective area epitaxy (SAE) which uses a mask either directly fabricated on or placed in contact with the substrate. During film deposition, epitaxial layers are grown on the substrate through apertures in the mask. In addition to selective area growth, SMMBE also produces a shadowing effect near the mask edges in which elemental fluxes vary as a function of position. This results in a gradient of film thickness and/or composition near the mask edges. The steepness of the gradient can be controlled by varying the mask thickness and/or the angle of the mask edges. In this paper, we demonstrate the potential of the SMMBE technique to create in-plane gradient permittivity materials (GPMs) by taking advantage of the shadowing effect. A GPM is a material in which the permittivity varies as a function of location. Our aim is to synthesize in-plane GPMs, in which the permittivity varies in the lateral in-plane direction rather than in the vertical growth direction. In an in-plane GPM, different wavelengths of light can be confined at different in-plane locations on the chip. We are interested in creating an infrared GPM, so we chose Si:InAs as our material. To create our GPMs, we use the SMMBE approach: by creating flux gradients of both indium and silicon near the edges of the mask, we can control the doping density and thus the permittivity of Si:InAs in the lateral in-plane direction. We started with reusable Si masks that are 200 um thick and 1 cm x 1 cm in dimension. Each mask has an aperture at its center which has a dimension of 0.5 cm x 0.5 cm at the top and 0.528 cm x 0.528 cm at the bottom. Nano-FTIR spectra obtained via s-SNOM using a mid-IR nano-FTIR module demonstrates that we successfully synthesized infrared GPMs. The GPM grown using a 200 um mask can confine light with wavenumbers 650 cm<sup>-1</sup> to 900 cm<sup>-1</sup> over an in-plane distance of 13 um. In this talk, I will discuss the

influence of several growth parameters in controlling the in-plane permittivity of the GPMs, including the growth temperature, mask thickness, and As:In ratio. In particular, the 500  $\mu\text{m}$  mask provides a larger shadowing effect in comparison to 200  $\mu\text{m}$  mask. This leads to a larger gradient in permittivity over a longer in-plane distance in the GPM: light with wavenumbers  $650\text{ cm}^{-1}$  to  $1400\text{ cm}^{-1}$  can be confined over an in-plane distance of 30  $\mu\text{m}$ . This provides a larger surface area for the construction of an ultracompact spectrometer. Tailored mask designs can be employed to synthesize in-plane GPMs with tailored permittivity gradients in the future.

9:00am **EM+2D+AP+QS+TF-ThM-5 Impact of Excess Ga on Electronic Properties in Plasma-assisted MBE-grown  $\beta\text{-Ga}_2\text{O}_3$ .** *Thaddeus Asel, B. Noesges, J. Li, Y. Kim, A. Neal, S. Mou*, Air Force Research Laboratory, Materials and Manufacturing Directorate, USA

$\beta\text{-Ga}_2\text{O}_3$  has been of significant interest due to its high electric breakdown field, commercially available native substrate, and shallow n-type donors. However,  $\beta\text{-Ga}_2\text{O}_3$  differs from other Ga-based semiconductors where metal-rich growth conditions are utilized to achieve adsorption-controlled growth by consuming the Ga flux entirely. Instead,  $\beta\text{-Ga}_2\text{O}_3$  growth must balance the incorporation of Ga with the desorption of a volatile suboxide species,  $\text{Ga}_2\text{O}$  where this suboxide is a limiting step when growing  $\beta\text{-Ga}_2\text{O}_3$  via molecular beam epitaxy (MBE) with a traditional Ga source. Increased  $\text{Ga}_2\text{O}$  desorption causes the growth rate of  $\beta\text{-Ga}_2\text{O}_3$  to decrease as the Ga flux is increased beyond the stoichiometric point of the material and can impact the stoichiometry of the grown film. In this work, we explore the impact of O-rich and Ga-rich conditions on electronic properties in films of  $\beta\text{-Ga}_2\text{O}_3$  grown via plasma-assisted MBE (PAMBE). Initial results comparing two samples under O-rich and Ga-rich conditions showed a large difference in peak low-temperature mobility. The O-rich sample showed a peak low temperature mobility of  $793\text{ cm}^2/\text{V}\cdot\text{s}$  while Ga-rich sample peaked at only  $198\text{ cm}^2/\text{V}\cdot\text{s}$ . The mobility and volume carrier density versus temperature data was fit using a model to extract out donor and compensating acceptor density. The Ga-rich sample showed an acceptor concentration of  $2.0\times 10^{16}\text{ cm}^{-3}$  compared to the O-rich sample that was measured to have an acceptor concentration of  $3.0\times 10^{15}$ , and order of magnitude lower. This is possibly due to the formation of  $V_{\text{Ga}}$  during the  $\text{Ga}_2\text{O}$  desorption process during the growth of the films. Another series of films were grown across a wider range of O- to Ga-rich conditions to further establish a trend between growth conditions and compensating acceptor density. Only Ga flux varied between samples and substrate temperature, Si source temperature and RF oxygen plasma conditions were held constant. Si concentration in each film was anti-correlated with the growth rate which is expected. Conversely, compensating acceptor density increased with increasing Ga-rich conditions and does not follow the trend of the growth rate. The best peak low-temperature mobility occurred for the sample grown in the most O-rich conditions ( $789.6\text{ cm}^2/\text{Vs}$ ) and mobility decreased with increasing compensating acceptor concentration. Overall, these results indicate the importance of Ga:O ratios in  $\beta\text{-Ga}_2\text{O}_3$  films grown via MBE with conventional Ga sources. These results demonstrate how improved electrical performance can be achieved in  $\beta\text{-Ga}_2\text{O}_3$  by growing under O-rich conditions and limiting the formation of  $V_{\text{Ga}}$  due to suboxide desorption.

9:15am **EM+2D+AP+QS+TF-ThM-6 Advancing Single-Crystalline Oxide Membrane Growth via Molecular Beam Epitaxy.** *Shivashesh Varshney, S. Choo*, University of Minnesota; *M. Ramis*, Institute of Materials Science of Barcelona (ICMAB-CSIC), Spain; *L. Thompson, J. Shah, Z. Yang, J. Wen, S. J. Koester, K. Mkhoyan, A. S. McLeod*, University of Minnesota; *M. Coll*, Institute of Materials Science of Barcelona (ICMAB-CSIC), Spain; *B. Jalan*, University of Minnesota

A sacrificial layer method has proven to be an effective route for synthesizing free-standing membranes. In this approach, a crystalline sacrificial layer is selectively dissolved in water, allowing the target film to be transferred onto a host substrate. However, commonly used sacrificial layers (such as  $\text{SrCa}_2\text{Al}_2\text{O}_6$ ) have complex stoichiometry, posing synthesis challenges in molecular beam epitaxy (MBE). In this presentation, we will discuss two distinct but MBE-friendly, fast and facile approaches to synthesize single-crystalline oxide nanomembranes using hybrid MBE [1,2]. In particular, we synthesize epitaxially, single-crystalline  $\text{SrTiO}_3$  membranes, ranging from a few unit cells to several hundred nanometers in thickness, using an  $\text{SrO}$  sacrificial layer, and a solution-processed amorphous  $\text{SrCa}_2\text{Al}_2\text{O}_6$  sacrificial layer. Films grow in a layer-by-layer growth mode on a solution-processed amorphous  $\text{SrCa}_2\text{Al}_2\text{O}_6$  whereas in a step-flow growth mode on  $\text{SrO}$  sacrificial layer. Films grown on  $\text{SrO}$  layer dissolve rapidly ( $< 5$  minutes) in water, resulting in millimeter-sized membranes. Combining

structural characterization using x-ray diffraction (XRD), atomic force microscopy (AFM), piezo force microscopy (PFM), and scanning transmission electron microscopy (STEM), we will present the structure-property relationships in these membranes with particular emphasis on investigating the role of non-stoichiometry on dielectric properties. Using PFM, we demonstrate that Sr-deficient films exhibit robust polarization at room temperature, while stoichiometric films remain consistent with the paraelectric phase. Finally, we will present the growth of single crystalline complex oxide films on a compliant substrate consisting of a few unit-cell  $\text{SrTiO}_3$  seed layers onto an amorphous  $\text{SiO}_2$  wafer.

1. S. Varshney, S. Choo, L. Thompson, Z. Yang, J. Shah, J. Wen, S. J. Koester, K. A. Mkhoyan, A. McLeod, and B. Jalan, "Hybrid Molecular Beam Epitaxy for Single Crystalline Oxide Membranes with Binary Oxide Sacrificial Layers" *ACS Nano* 8, 18, 6348-6358 (2024).
2. S. Varshney, M. Ramis, S. Choo, M. Coll, and B. Jalan, "Epitaxially Grown Single-Crystalline  $\text{SrTiO}_3$  Membranes Using a Solution-Processed, Amorphous  $\text{SrCa}_2\text{Al}_2\text{O}_6$  Sacrificial Layer" under review (2024) <http://arxiv.org/abs/2405.10464>

## Thin Films

### Room 115 - Session TF1+AP-ThM

#### Thin Films: Fundamentals of ALD

Moderators: Matthias Young, University of Missouri, Sarah Atanasov, Intel

8:00am **TF1+AP-ThM-1 AVS Medard W. Welch Award Talk: The Surface Chemistry of the Atomic Layer Deposition of Metal Thin Films.** *Francisco Zaera*<sup>1</sup>, University of California - Riverside **INVITED**

The deposition of thin solid films is central to many industrial applications, and, thanks to the isotropic nature of the adsorption of chemical species (which affords even coverages on surfaces with rough topographies), chemical vapor deposition (CVD) methods are particularly useful for this task. Moreover, by splitting the overall film-depositing reactions into two or more complementary and self-limiting steps, as it is done in atomic layer depositions (ALD), film thicknesses can be controlled down to the sub-monolayer level. Thanks to the availability of a vast array of inorganic and metalorganic precursors, CVD and ALD are quite versatile and can be engineered to deposit virtually any type of solid material. However, the surface chemistry that takes place in these processes is often complex and can follow undesirable side reactions leading to the incorporation of impurities in the growing films. Appropriate precursors and deposition conditions need to be chosen to minimize these problems, and that requires a proper understanding of the underlying surface chemistry.

In this presentation we discuss the progress made in our laboratory toward that goal. Our focus has been on the deposition of late transition metals. We will comment on the general nature of the metalorganic complexes used as precursors for these depositions, and the uniqueness that solid surfaces and the absence of liquid solvents bring to the ALD chemistry and differentiate it from what is known from metalorganic chemistry in solution. We then delve into the adsorption and thermal chemistry of those precursors, highlighting the complex and stepwise nature of the decomposition of the organic ligands that usually ensued upon their thermal activation. We discuss the criteria relevant for the selection of co-reactants to be used on the second half of the ALD cycle, with emphasis on the redox chemistry often associated with the growth of metallic films starting from complexes with metal cations. Another consideration is the nature of the growing films, which rarely retain the homogeneous 2D structure often aimed for. We end with some general conclusion and with a personal outlook of this field.

8:30am **TF1+AP-ThM-3 Effects of ALD Chemistry on Process Windows, Thin Film Composition and Modification of the Underlying Substrate Surface.** *Jay Swarup, J. Engstrom*, Cornell University

In this work we have examined explicitly how the choice of ALD chemistry (precursor and co-reactant) can affect the process temperature window, composition of the deposited thin film, and possible modification of the underlying substrate. Growth of  $\text{Al}_2\text{O}_3$  from  $\text{Al}(\text{CH}_3)_3$  (TMA) and  $\text{H}_2\text{O}$  may be the most studied and robust ALD process. Here we consider two perturbations from this benchmark process by considering both a different precursor (a heteroleptic Al complex, void of halogens and Al-C bonds,  $\text{L}_2\text{Al}^{\text{L}}$ ), and a different organic oxidizing compound ( $\text{RO}_x$ ). We have

<sup>1</sup> Medard W. Welch Award Winner

employed a quartz-crystal microbalance (QCM) to monitor ALD *in situ* and in real-time, and the deposited thin films have been characterized using X-ray photoelectron spectroscopy, spectroscopic ellipsometry, and X-ray reflectivity. Growth of thin films of Al<sub>2</sub>O<sub>3</sub> using TMA and either RO<sub>x</sub> or H<sub>2</sub>O as the co-reactant at  $T = 285$  °C produces thin films of similar physical properties (density, stoichiometry, minimal carbon incorporation), and the growth rate per cycle is similar for the two co-reactants at this temperature. At a lower temperature of  $T = 120$  °C, the behavior is starkly different, where growth occurs with H<sub>2</sub>O but not with RO<sub>x</sub>. At either process temperature, we find no evidence for significant coverages of a long-lived intermediate from the reaction of RO<sub>x</sub>. Growth from the heteroleptic Al precursor is similar to that observed with TMA—essentially stoichiometric Al<sub>2</sub>O<sub>3</sub> is formed, and growth occurs readily with H<sub>2</sub>O at  $T = 120$  and  $285$  °C, while there are differences in the species formed at the end of the precursor half cycle. Growth with the heteroleptic precursor and the organic oxidizing species exhibits a similar dependence on temperature as observed with TMA—deposition at  $T = 285$  °C, but not at  $T = 120$  °C. Deposition of thin films of Al<sub>2</sub>O<sub>3</sub> on metal surfaces of Cu and Co has been examined for evidence of interfacial oxidation.<sup>[1]</sup> While growth with either co-reactant (H<sub>2</sub>O or RO<sub>x</sub>) does not lead to the oxidation of the underlying Cu substrate, use of H<sub>2</sub>O leads to the oxidation of Co, while use of RO<sub>x</sub> as the co-reactant does not. We postulate that the size of the co-reactant in this case plays a role, where the diffusion of species through the deposited Al<sub>2</sub>O<sub>3</sub> thin film could result in oxidation at the Al<sub>2</sub>O<sub>3</sub>/metal interface, a process that is strongly hindered in the case of RO<sub>x</sub> due to its size.

[1] *ACS Appl. Mater. Interfaces* **16**, 16983–16995 (2024).

## 8:45am TF1+AP-ThM-4 Atomic Layer Deposition Chemistry – Trimethylaluminum on SiO<sub>2</sub> and Cu from a Surface Science Perspective, Leonhard Winter, F. Zaera, University of California, Riverside

Atomic Layer Deposition (ALD) is a chemical method used to grow thin films by sequentially employing complementary, self-limiting half-reactions. ALD offers the possibility to grow high-quality films on geometrically challenging substrates with sub-monolayer thickness control. An important development in ALD research is the ability to perform the growth selectively on specific areas.<sup>[1]</sup> For example, in the microelectronics industry, an ALD film often needs to be grown only on the dielectric (often SiO<sub>2</sub>) or only on the electric contacts (often Cu) while avoiding the other material. Therefore, it is important to understand the surface chemistry of the ALD precursors on the competing surfaces. There has been some progress towards this goal,<sup>[2]</sup> but more mechanistic details are needed to tailor the selective ALD chemistry. To this end, we have set to first study and contrast the surface chemistry of trimethylaluminum (TMA), a precursor commonly used to deposit Al<sub>2</sub>O<sub>3</sub> films, on SiO<sub>2</sub> versus Cu surfaces by using X-ray photoelectron spectroscopy (XPS) and temperature-programmed desorption (TPD). On SiO<sub>2</sub>, we have observed high chemical reactivity of this precursor at unexpectedly low temperatures and exposures, below the cryogenic temperatures required for multilayer condensation. This low-temperature chemistry appears to be complex, with desorption of Al-containing fragments being accompanied with changes in the relative Al/C atomic ratio on the surface. It was also determined that the initial sticking coefficient at room temperature is approximately 4-5 times smaller than at cryogenic temperatures, and that the TMA uptake is self-limiting. This high TMA reactivity on SiO<sub>2</sub> surfaces will need to be compared with that on Cu substrates, as the differences are expected to have significant implications for the selectivity of the ALD and for strategies to control it.

[1] A. J. M. Mackus, M. J. M. Merckx, W. M. M. Kessels, *Chem. Mater.* **2018**, *31*, 2-12.

[2] S. T. Barry, A. V. Teplyakov, F. Zaera, *Acc. Chem. Res.* **2018**, *51*, 800-809.

## 9:00am TF1+AP-ThM-5 Spatial Atomic Layer Deposition: Transport-Reaction Modeling and Experimental Validation of Film Geometry, Daniel Penley, N. Dasgupta, University of Michigan, Ann Arbor

Close-proximity atmospheric-pressure spatial atomic layer deposition (AP-SALD) is a powerful technique to control nanoscale surfaces and interfaces at scales relevant to large-scale manufacturing. To investigate the manufacturing tradeoffs in an AP-SALD system (film quality-throughput-cost-sustainability), many studies utilize computational modeling to gain insight into the difficult to observe process region that contains the isolated precursor zones. However, there is limited investigation into the effects of process parameters on the spatial separation and distribution of the

precursor zones and their resulting impact on the deposited film. Additionally, few previous works have paired a computational model with an experimental system that has comparable, closed-loop control over the many system parameters, including gap size, relative alignment, gas flow rates, and substrate velocity.

In this work, we introduce a transport-reaction model to study how variations in process parameters affect the resulting deposited film. A finite element method model uses laminar flow fluid mechanics and transport of dilute species to give insight into the pressure, velocity, and partial pressure gradients within the process region. These outputs are then input into a surface reaction model that simulates the chemical reactions, yielding predicted film thickness maps. The model is validated and parameterized by comparing the simulated film geometries with TiO<sub>2</sub> films deposited using a mechatronic AP-SALD system. By coupling an experimental system with the transport-reaction model, process parameters can be tuned both physically and digitally to provide new insights into AP-SALD process control and optimization for thin film deposition at large scales.

## 9:15am TF1+AP-ThM-6 Deposition Efficiency Modeling according to Precursor Flow Rate in ALD Process with Fixed Chamber Pressure, Dongho Shin, Samsung Electronics, Republic of Korea

Atomic Layer Deposition (ALD) is a key technology for achieving excellent thin film step coverage in a high aspect ratio structure. Therefore, many studies regarding various ALD technologies and ALD mechanism modeling in microstructure have been conducted. However, there are few studies of ALD technologies in terms of cost and environment, related to the efficiency of precursor used during ALD process. Deposition Efficiency (DE) is defined as the ratio of the thickness of deposited film to the volume of the precursor consumed. Research on ALD technologies that reduce precursor consumption by increasing DE of precursor is urgently needed considering cost reduction and ESG management. Therefore, in this paper, a new precursor supply model representing DE is established for ALD system with fixed pressure control. Based on the model, we found that precursor flow rate and DE are inversely proportional. Due to this characteristic, the decrease of the flow rate results in the higher DE. The feasibility of the model has been confirmed through CFD simulation and the model is finally verified through pattern evaluation. This proposed concept presents an additional direction to be pursued in ALD research in the future.

## 9:30am TF1+AP-ThM-7 Time-Resolved Heat Generation of ALD MgO Surface Reactions, Ashley Bielinski, J. Xu, Argonne National Laboratory; S. Htun, Northwestern University; S. Hruszkewycz, C. Liu, A. Martinson, Argonne National Laboratory

Many of the properties that are prized in films deposited with atomic layer deposition (ALD) such as precise control of composition and thickness, as well as conformal coverage on high aspect ratio structures, rely on the self-limiting nature of ALD surface reactions. A deeper understanding of the fundamental thermodynamics, kinetics, and mechanisms of ALD precursor reactions is essential to enable emerging applications such as site-selective ALD and area-selective ALD, which rely on chemical selectivity between precursor molecules, inhibitors, and the substrate surface. Differences in the surface composition and availability of reactive sites, as well as the precursor ligands can have a significant influence on the properties of the deposited film and the formation of interfaces, even within a given material system.

ALD pyroelectric calorimetry measures the *in situ*, time-resolved heat generated by ALD surface reactions under standard ALD conditions. Previously, we used this technique to measure the heat generation rates of trimethylaluminum (TMA), tetrakis(dimethylamino)zirconium (TDMAZr) and water to form Al<sub>2</sub>O<sub>3</sub> and ZrO<sub>2</sub>. Here we extend this technique to study the reaction between bis(ethylcyclopentadienyl)magnesium (Mg(CpEt)<sub>2</sub>) and water to form MgO. To fully extract the heat generated by these ALD surface reactions over longer time scales, the data was fit to a calibrated model to account for cooling and electronic decay. These results were then compared to computational first principles models of various surfaces and reaction steps as well as calculations of the standard reaction enthalpies. Pyroelectric calorimetry provides a unique opportunity to quantitatively benchmark the values provided by computational models. This can help evaluate the accuracy of proposed processes and mechanisms. Heat generation rates provide new insight into ALD processes, helping us to untangle the thermodynamics, kinetics, and mechanisms of these heterogeneous surface reactions.

# Thursday Morning, November 7, 2024

9:45am TF1+AP-ThM-8 **In situ Stress Measurements During Tungsten Atomic Layer Deposition**, *Ryan B. Vanfleet, S. George*, University of Colorado at Boulder

*In situ* film and surface stresses were measured during tungsten (W) atomic layer deposition (ALD) using wafer curvature techniques. Tungsten was deposited at temperatures between 130 °C and 300 °C using tungsten hexafluoride (WF<sub>6</sub>) and disilane (Si<sub>2</sub>H<sub>6</sub>) as the reactants on aluminum oxide (Al<sub>2</sub>O<sub>3</sub>) ALD surfaces. The stress was initially compressive during nucleation over the first 8-10 W ALD cycles as expected from a Volmer-Weber growth model. The stress was then tensile as the film became continuous.

Large tensile stresses were measured for the W ALD films. The film stress was ~2.0 GPa at a deposition temperature of 200 °C (Figure 1). For comparison, Al<sub>2</sub>O<sub>3</sub> ALD films deposited at low temperatures have much smaller tensile film stresses of ~0.45 GPa. The large tensile stress in W ALD films may be generated at the grain boundaries. Atoms are too far apart at grain boundaries and experience an attractive force that wants to pull them together.

Surface stresses were also measured during the individual WF<sub>6</sub> and Si<sub>2</sub>H<sub>6</sub> exposures (Figure 2). The WF<sub>6</sub> exposures produce a tensile stress of ~+2 N/m. This tensile stress is correlated with WF<sub>6</sub> reacting with SiF<sub>2</sub>H\* sacrificial surface species to deposit WF<sub>5</sub>\* surface species (SiF<sub>2</sub>H\* + WF<sub>6</sub>(g) -> WF<sub>5</sub>\* + SiF<sub>3</sub>H(g)). The Si<sub>2</sub>H<sub>6</sub> exposures then partially release the tensile stress with a stress change of ~-1 N/m. The Si<sub>2</sub>H<sub>6</sub> exposures redeposit SiF<sub>2</sub>H\* sacrificial surface species (WF<sub>5</sub>\* + Si<sub>2</sub>H<sub>6</sub>(g) -> WSiF<sub>2</sub>H\* + SiF<sub>3</sub>H(g) + 2H<sub>2</sub>(g)).

The large tensile stress in the W ALD films can lead to film cracking and delamination. This phenomenon is clearly evidenced by the *in situ* stress measurements (Figure 3). A large reduction in tensile stress is observed during film failure. The film failure was also obvious by visual inspection of the W ALD films when the W films began to peel off the underlying wafer.

Additional *in situ* measurements have observed that the large tensile film stress in W ALD films may be reduced by occasional exposures to trimethylaluminum (TMA). The addition of Al breaks the crystalline continuity in the W ALD film and forces the W ALD film to re-nucleate. These observations suggest that film stress can be controlled by adding dopants during film growth.

## Atomic Scale Processing Mini-Symposium Room Central Hall - Session AP-ThP

### Atomic Scale Processing Mini-Symposium Poster Session

#### AP-ThP-1 Surface Bromination as a Way to Prepare an Atomic-Layer Resist: A Path Towards Area-Selective Deposition, *John R. Mason, A. Teplyakov*, University of Delaware

As the size of components in electronics is shrinking, and their designs continue to get more complex, we need to find new approaches to meet these design needs. Area-selective atomic layer deposition is a rising technology to address the requirement for reaching single-nanometer sized features, while keeping the high uniformity that is desired. Silicon bromination has been demonstrated to produce a surface that can effectively resist metal oxide deposition; however, such a substrate is difficult to prepare outside of ultra-high vacuum conditions. This study aims to provide alternative methods for brominating silicon (100) wafers without the need for expensive ultra-high vacuum equipment, with strong ability to resist deposition of titanium dioxide. The study looks at various bromine-based chemistries in liquid phase to prepare a non-growth surface and compares the resulting selectivity for TiO<sub>2</sub> deposition using titanium tetrachloride or tetrakis(dimethylamido)titanium as a titanium source and water as the oxygen source. The process is compared with that on the traditional non-growth surface of hydrogen-terminated silicon and on the traditional growth surface of oxidized silicon.

Surface morphology is monitored with atomic force microscopy and scanning electron microscopy. Atomic concentrations are followed with X-ray photoelectron spectroscopy to observe surface ability to serve as a resist. In addition, the deposition process, the chemical environment of the inhibitor species, and the thickness of the ultimately deposited oxide layers are observed using TOF-SIMS.

#### AP-ThP-2 Thermal Atomic Layer Etching Process for 2D van der Waals Material CrPS<sub>4</sub>, *Marissa Pina, M. Whalen, J. Xiao, A. Teplyakov*, University of Delaware

CrPS<sub>4</sub> is a 2D van der Waals ternary transition metal chalcogenide (TTMC). CrPS<sub>4</sub> is an A-type antiferromagnetic semiconductor, in which spins within the same layer are aligned in same direction but spins in adjacent layers are aligned in opposite directions. Ferromagnetic and antiferromagnetic orderings are observed within the same layer and between adjacent layers, respectively. Consequently, thin flakes a few layers thick can display net or zero magnetization depending on whether there is an odd or even number of layers.

In order to understand the magnetism down to the monolayer limit and the dynamic excitations in magnons and excitons, and make devices based on 2D magnetic materials viable for industry, 2D materials with well-controlled layer structures have to be produced. The existing methods for controlling CrPS<sub>4</sub> thickness, such as mechanical and liquid exfoliation, are either not well controlled or introduce damage to the crystal structure. In this study, we will show that thermal atomic layer etching (ALE) can be used to controllably etch the 2D crystals of this material without contaminating them. Ultimately, using ALE to manipulate the thicknesses of these flakes will allow for controlling their magnetic and dynamic optical properties.

CrPS<sub>4</sub> flakes were exfoliated onto a gold film from a single crystal via mechanical exfoliation. Thermal ALE cycles were performed in an ultra-high vacuum chamber. Each cycle was performed at elevated temperature and consisted of a chlorine dose using a solid-state electrochemical chlorine source followed by an acetylacetone dose. Atomic force microscopy was used to determine an average etching rate of 0.10 ± 0.07 nm/cycle. Although the etching rate appeared to depend on the thickness of the flakes, this average removal rate was recorded for 75 different points for flakes ranging from 4 to 90 nm in thickness. ALE also removed the island defects caused by exfoliation from the top of the flakes. XPS and ToF-SIMS were used to follow chemical changes in the material and to interrogate the distribution of etchant components within the flakes. The formation of chemical species containing acetylacetone ligands was confirmed for all the components (Cr, P, S) of this TTMC, and the chlorination was followed in ToF-SIMS depth-profiling experiments. The ALE process that resulted in controlled material removal did not result in measurable surface contamination. Importantly, the etching of CrPS<sub>4</sub> is highly temperature-dependent, as lowering the process temperature by even 30 °C does not result in noticeable etching. Further, faster etching (above ALE regime) can be achieved using higher temperatures and higher pressures.

#### AP-ThP-3 Conversion of TiO<sub>2</sub> ALD Precursor Selectivity via Amination of Chlorinated Silicon with Primary Amines, *Tyler Parke, J. Mason, A. Teplyakov*, University of Delaware

Area-selective atomic layer deposition (AS-ALD) is a rapidly developing technique which allows for the fabrication of 3D nanoelectronic architectures. AS-ALD schemes may be made more versatile by introducing surface modification steps which 'switch' non-growth surfaces, which are unreactive to ALD precursors, to reactive growth surfaces. While several studies have demonstrated the conversion of chlorine- or hydrogen-terminated silicon to amino-terminated silicon, both in solution and gas-phase reactions, few have focused on the subsequent use of these prepared surfaces as ALD substrates. Chlorinated silicon resists were modified in vacuo with ammonia and methylamine to produce amino surface ligands and TiO<sub>2</sub> ALD was performed on each resulting surface to test its reactivity as a growth or non-growth surface in the presence of titanium tetrachloride or tetrakis(dimethylamino)titanium (TDMAT). Deposition was confirmed by XPS and surface species resulting from reaction of titanium precursors on each surface were probed with in situ FTIR and ex situ time-of-flight secondary ion mass spectrometry (ToF-SIMS). The experimental surface species data was paired with density functional theory (DFT) simulations of the local surface structure to propose a reaction pathway.

#### AP-ThP-4 Atomic Layer Deposition of Ruthenium and Ruthenium Oxide Thin Films for Electrochemical Water Splitting, *Swapnil Nalawade, D. Kumar, S. Aravamudhan*, North Carolina A&T State University

Electrochemical water splitting is a unique and sustainable hydrogen production cycle with water and oxygen as the only by-products. However, at present, the primary hurdle for hydrogen production from water is the lack of materials that can support the reaction with high efficiency. Addressing the hydrogen challenge requires innovations in catalysis for the oxygen evolution reaction (OER) and hydrogen evolution reaction (HER), the two electrochemical reactions in water splitting. Among the many electrocatalysts, thin films of Ruthenium and Ruthenium Oxide for OER and HER are very promising because of their high catalytic activity, broad pH applicability and long-term stability. In this work, we studied as-grown and post-annealed properties of Ruthenium and Ruthenium Oxide thin films deposited by thermal atomic layer deposition (ALD) technique. ALD Ru films were deposited at 300C using Ru(EthylCycloPentaDienyl)<sub>2</sub> and oxygen as co-reactants and characterized for morphology, composition, and resistivity. Post-annealing at higher temperatures (400-600C) in oxygen environment resulted in phase transformation of the as-grown Ru to RuO<sub>2</sub>. These phase changes were confirmed using XRD, XPS, Raman and resistivity measurements. Finally, repetitive redox cycling (electrochemical studies) were conducted to study thin film stability and polarization behavior.

#### AP-ThP-5 Fabrication of p-n Junction Photodiodes using Low-Temperature ALD grown ZnO and NiO films on Si substrates, *H. Jiang, T. Cu, S. Bin Hafiz, H. Saleh, F. Bayansal, I. Sifat, A. Agrios, Necmi BIYIKLI*, University of Connecticut

In this study, we present findings on the photodiodes made of ALD grown ZnO and NiO films. The ZnO deposition process on p-type Si substrate samples involved the use of diethylzinc as the metal precursor and H<sub>2</sub>O as the co-reactant. The thermal ALD deposition was done at 120 °C with 20 sccm of N<sub>2</sub> flow, 500 ms pulse time for 400 cycles. The thickness of ZnO film was measured as ~48 nm. On the other hand, NiO deposition on n-type Si substrate samples required nickelocene (bis(cyclopentadienyl)nickel) as precursor and O<sub>2</sub> plasma as co-reactant. The plasma-ALD process was conducted at 200 °C with 100W RF plasma power. The plasma duration was 20 seconds and total deposition run was 800 cycles. The resulting thickness of NiO film was ~34 nm.

The p-n photodiode device layout was similar to the design of a commercial solar cell with interdigitated electrode metal contacts. We designed 1 x 1 cm devices, in which we used 5/5 μm finger-width/spacing to collect generated photocurrent. After metal-oxide deposition, we fabricated the patterned contact metals via photolithography and lift-off process. 20/30 nm Ti/Al metal layers were e-beam evaporated on n-ZnO/p-Si and p-NiO/n-Si samples. The samples were then soaked in remover solution where metal lift-off process was completed with ultrasonication.

The I-V curves of ZnO/Si and NiO/Si devices show typical characteristics of back-to-back Schottky-diode and p-n junction photodiode, respectively. ZnO/Si Schottky photodiodes typically display rectifying behavior, showing minimal current flow under reverse bias due to the presence of a Schottky barrier, followed by a steep increase in reverse current beyond the barrier height. Under forward bias, rectifying behavior is observed, with a turn-on

voltage indicating the onset of conduction. For NiO/Si p-n junction photodiode, the curve exhibits a clear rectifying behavior with exponentially increasing current at positive bias voltage, signaling unhindered current flow. Conversely, minimal current is observed under negative reverse bias voltages. These initial results indicate promise in achieving high-performance UV photodetector characteristics using both as-grown crystalline n-type ZnO and p-type NiO layers grown via thermal and plasma-assisted ALD, respectively at substrate temperatures less than 200 °C.

**AP-ThP-6 Design of Gas Flow Field for a Microchannel Flow ALD Processing Chamber**, *Kyung-Hoon Yoo*, Korea Institute of Industrial Technology, Republic of Korea; *G. Song*, KUMYOUNG ENG Inc., Republic of Korea; *C. Kim*, TNG Co., Republic of Korea; *J. Hwang, H. Lee, S. Lee, J. Woo*, Korea Institute of Industrial Technology, Republic of Korea; *K. Lee*, Samasung Display, Republic of Korea

It is necessary to establish a sustainable manufacturing technology for a high-productivity, high-efficiency ALD processing chamber and cluster tool that reduce the intrinsic excessive consumption of energy and materials because semiconductor ALD processes can be a concern for economic and environmental feasibility.<sup>1,2</sup> In the present study, as the part of countermeasure to the excessive consumption, a microchannel flow ALD processing chamber is considered for the optimized design with the process space volume decreased. The changes in the flow field of nitrogen in the process space of the processing chamber with the gap size of 1 mm or 10 mm respectively are observed at 400 °C, utilizing computational fluid CFD numerical analysis. For the present nitrogen flow field with a inlet static pressure of 1 or 10 Torr and a inlet mass flowrate of  $4.233 \cdot 10^{-6}$ , the Knudsen number  $Kn=0.223$  and Reynolds number  $Re=1.474$  are evaluated. The continuity, momentum and energy equations of a steady-state compressible laminar flow field are considered.<sup>3,4</sup>

#### Acknowledgment

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#### References

1. C.Y. Yuan and D.A. Dornfeld, *J. of Manufacturing Science and Engineering* **132**, 030918 (2010).
2. E. J. McInerney, *J. Vac. Sci. Technol. A* **35**, 01B138 (2017).
3. M. R. Shaeri, T.-C. Jen, C. Y. Yuan and M. Behnia, *International Journal of Heat and Mass Transfer* **89**, 468 (2015).
4. D. Pan, L. Ma, Y Xie, T.C. Jen and C. Yuan, *J. Vac. Sci. Technol. A* **33**, 021511 (2015).

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