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. Merkx, 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_2 and TiN films. On various substrates, a thin SiO_2 overlayer deposited by ALD was exposed to low-energy Ar ions (33-50 eV). The amount of SiO_2 removed depends significantly on the substrate (Al_2O_3, TiO_2, Nb_2O_5, MoO_3, HfO_2, Ta_2O_5, and WO_3 were investigated here). In general, the heavier the mass of the metal atoms in the substrate, the less SiO_2 is observed after the ion exposure. TiN was selectively deposited on Al_2O_3 with respect to a HfO_2 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_2O_3 with only 0.15 nm on HfO_2 (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_2 Functionalization with Methyl versus Silyl Groups to Enable Area-Selective Atomic Layer Deposition of Al_2O_3*, 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_2 films are extensively used in semiconductor manufacturing. Area-selective atomic layer deposition (AS-ALD) of a dielectric, such as Al_2O_3, on a target surface with SiO_2 as a non-growth surface, can simplify device processing. Gas-phase functionalization of SiO_2 using aminosilanes as small molecule inhibitors has been previously reported. Most studies show that growth nucleation during ALD occurs on the functionalized SiO_2 surface after just a few nanometers of deposition on the growth surface. It is speculated that nucleation on the SiO_2 surface occurs due to the availability of unreacted surface –SiOH groups. We tested this hypothesis by functionalizing the SiO_2 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_2 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 $–Si(CH_3)_3$ and $–SiH_3$ 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_2 surface: these –SiOH groups became available for reaction with dimethylaluminum isopropoxide (DMAI) during Al_2O_3 ALD. In contrast, *in situ* 4-wavelength ellipsometry shows that functionalization of the as-deposited SiO_2 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_2 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_2O did not react with surface $–SiH_3$ or $–Si(CH_3)_3$ 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 $–Si(CH_3)_3$ ligand, there is a still a nucleation delay on the pre-annealed SiO_2 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 $(\eta^3\text{-allyl})Ru(CO)_3X$ (X = Cl, Br, I) precursors. Three SAMs were employed with $–CH_3$, –OH or –COOH terminal groups. Under UV light using $(\eta^3\text{-allyl})Ru(CO)_3Br$ we showed that Ru(0) and RuO_x selectively deposits on $–CH_3$ 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 $(\eta^3\text{-allyl})Ru(CO)_3X$ (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 $(\eta^4\text{-diene})Ru(CO)_3$ (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 $(\eta^3\text{-allyl})Ru(CO)_3Br$ 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 $–CH_3$ and –OH terminated SAMs.

9:30am **AP+EM+PS+TF-MoM-6 A Stochastic Lattice Deposition Model for Visualization of ALD and Area-Selective Deposition of Metal Oxides***, **Nicholas Carroll**, G. Parsons,* North Carolina State University

Area-selective deposition (ASD) is of interest to augment advanced lithographic patterning to achieve improved resolution and feature alignment. In addition to controlled substrate-dependent nucleation and growth, precise feature alignment will also require understanding and ability to adjust the lateral growth of ASD materials, for example, to control lateral "mushrooming". Previous analytical models give insight into trends in thickness, selectivity, surface coverage, and areal nuclei density during ASD, but models capable of visualizing and analyzing lateral over-growth for various ASD processes are not as well known. In this work we describe a stochastic lattice deposition model capable of simulating atomic layer deposition (ALD) and ASD of metal oxide films with nucleation in a localized "growth" region and lateral over-growth of the film into an optional "non-growth" region. ALD cycles are simulated using a set of reactive sites (*i.e.* a hydroxyl group) that interact with an incoming precursor (*i.e.* trimethylaluminum) to produce randomly arranged metal and ligand sites on a 3D cubic grid lattice. The metal center binds to the oxygen site, and the remaining ligand groups are oriented adjacent to the metal center. The stoichiometry, density, and OH concentration in the resulting film can be tuned to experimentally reasonable values by implementing adjustments to the extent of packing and bridge-site reactivity during the ALD cycle. Using well-controlled ALD conditions, the model allows the extent of lateral growth over adjacent "non-growth" regions to be observed and quantified. To adjust the extent and shape of lateral growth, several parameters were considered, including enhanced attractive interactions between precursors and the non-growth substrate surface, localized substrate oxidation at the leading edge of the film, and others. We have also begun to use the model to consider the influence of non-planar substrate geometry in the extent of ASD. Results from model output will be compared to published experimental results, giving insights into possible physical and chemical mechanisms driving non-uniform ALD and ASD.

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_3 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/H2 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 AlOx 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

10:00am **AP+EM+PS+TF-MoM-8 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_2 deposition is performed using thermal ALD with tetrakisdimethylamidotitanium (TDMAT) or $TiCl_4$ 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).

10:30am **AP+EM+PS+TF-MoM-10 Selectivity Loss During Area-Selective Deposition Processes: The Role of Chemical Passivation and Steric Shielding***, M. Merkx, P. Yu, I. Tezsevin, A. Mackus,* Eindhoven University of Technology, Dept. Applied Physics, Netherlands*; **Tania E. Sandoval**,* 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. Merkx, 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. Tezzevin, P. Yu, M. Merkx,* TU / Eindhoven, Netherlands*; T. Sandoval,* Universidad Tecnica Federico Santa Maria, 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.[1] 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.[2] 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, 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 Al_2O_3, SiO_2, AlN, and Si_3N_4 using this method; surfaces chosen for their applications in semiconductor industry (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, acetadiimidine, and imidodicarbonic diamide are promising candidates to be use 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. Merkx,* Eindhoven University of Technology, Netherlands*; S. Semproni, J. Chen,* Intel Corporation*; T. Sandoval,* Universidad Técnica Federico Santa Mariá, 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.[1,2] 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 ($C_4H_4N_2$), which exhibits strong adsorption on Cu via its nitrogen atoms. Random sequential adsorption simulations[3] of pyridazine on Cu show that it can densely pack on the surface with a surface density of more than 2.4 molecules per 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) Merkx, 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. Merkx, J. Maas, I. Tezsevin, W. Kessels,* Eindhoven University of Technology, The Netherlands*; T. Sandoval,* Universidad Tecnica Federico Santa Maria, 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 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 (H_2 and O_2) exposure (steps D and C) were carried out on the non-growth area Al_2O_3. RAIRS spectra were taken after the steps A, B, and DC. We learned in previous work that the adsorption of Hacac on Al_2O_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 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. Merkx *et al.*, *Chem. Mater.* **32**, 3335–3345 (2020).

[3] M. J. M. Merkx *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, SiO_2, and TiN, respectively. These inhibitors display selective adsorption on the Cu surface and in some cases on the 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 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 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.

Thin Films
Room 115 - Session TF1-MoM
Thin Films for Energy Applications I: Green Fuels and Photovoltaics

Moderators: Alexander Kozen, University of Vermont, **Blake Nuwayhid**, Naval Research Laboratory

8:15am **TF1-MoM-1 Unravelling the Role of Stoichiometry of ALD Oxygen Evolution Electrocatalysts on Their Activity**, ***Mariadriana Creatore***, Eindhoven University of Technology, The Netherlands **INVITED**

Production of green hydrogen is a key contributor to the energy transition, and the synthesis of cost-effective, earth-abundant oxygen evolution reaction (OER) electrocatalysts for H_2O splitting is presently subject of major investigation.In this contribution I will address the synthesis of two electrocatalysts, i.e., cobalt phosphate (CoPi) and nickel cobalt oxide (NCO), by plasma-assisted atomic layer deposition and discuss the merit of digital control over film stoichiometry to generate insight on the activation mechanisms of these electrocatalysts.

CoPi is prepared by combining ALD cycles of CoO_x from cobaltocene ($CoCp_2$) and O_2 plasma, with cycles of trimethylphosphate ($(CH_3O)_3PO$) followed by O_2 plasma. We show that the CoPi films undergo activation with increasing number of cyclic voltammetry (CV) cycles. During activation, the current density increases in parallel with a progressive leaching of phosphorous out of CoPi. These chemical changes proceed along with structural changes: measurements of the electrochemical surface area (ECSA) reveal that during activation, the ECSA of the film increases and that the electrochemical activity scales linearly with ECSA for all film compositions. Thus, the initial composition indirectly affects the activity of the catalyst by steering its restructuring during cycling and the ECSA is the sole parameter determining the activity of CoPi.

The second study addresses an ALD super-cycle based on $CoCp_2$ and nickel methylcyclopentadienyl ($Ni(^{Me}Cp)_2$) and an O_2 plasma. We observe a phase transition from Ni-rich rock-salt films to Co-rich spinel films at ~55 at.% Co. The transition is accompanied by an increase in the +3-to-+2 oxidation state ratio of the metal centers. Electrochemical analysis discloses a synergistic effect between Co and Ni metal centers, such that NCO films are more OER-active than Co_3O_4 and NiO. Moreover, rock-salt films continuously form an hydroxide phase during CV cycling, resulting in prolonged activation such that an optimal overpotential of 470 mV is observed for the 30 at.% Co film after 500 cycles. Instead, the presence of Co limits the bulk hydroxide formation, such that a constant performance at an overpotential of ~500 mV is observed for the spinel films. The activation process occurs in parallel with an increase in ECSA up to a factor 8 for rock-salt films. The improved OER activity of rock-salt films upon electrochemical activation indicates that the low-cobalt content films are a sustainable alternative to the more commonly investigated cobalt-rich films.

8:45am **TF1-MoM-3 Stability of $CsPbBr_3$ Employing an Ultrathin Al_2O_3 Protective Layer**, *F. Quintero-Borbon,* Centro de Investigación en Materiales Avanzados SC, Unidad Monterrey, Mexico*; J. Roy, L. Izquierdo-Fernandez,, R. Wallace, M. Quevedo-Lopez,* Department of Material Science and Engineering, University of Texas at Dallas*;* ***Francisco S. Aguirre-Tostado,*** Centro de Investigación en Materiales Avanzados SC, Unidad Monterrey, Mexico

Lead halide perovskite nanocrystals, such as $CsPbBr_3$, have gathered significant interest due to their attractive optical properties and cost-effective production. However, their environmental stability remains a major challenge, hindering practical applications and scalability for commercialization. In this study, we propose an effective method to enhance the stability of $CsPbBr_3$ by depositing an ultrathin Al_2O_3film using atomic layer deposition (ALD). The $CsPbBr_3$ was deposited on a glass substrate using closed space sublimation (CSS) from a 1:1 molarratio of PbBr2 and CsBr previusly mix powders. The $Al_2O_3$was deposited from a TMA and H_2O suources using thermal ALD. This unique single layer protection structure significantly improves their resistance to moisture, and polar solvents. Notably, the modified surface exhibits chemical stability and stable photoluminescence (PL) intensity compared to the ordinary $CsPbBr_3$ surface. Additionally, Xray photoelectron spectroscopy analysis shows a chemically abrupt $Al_2O_3/CsPbBr_3$ interface with high stability with respect to the water-soaked $CsPbBr_3$ surface. This research presents a promising approach for developing stable perovskite thin films with enhanced performance in various optoelectronic devices.

9:00am **TF1-MoM-4 Deposition of Yb-doped Double Halide Perovskite $Cs_2AgBiCl_6$ for High-Efficiency Downconversion of Ultraviolet Photons**, ***Pulkita Jain**, M. Tran, I. Cleveland, Y. Liu, S. Sarp, E. Aydil,* New York University

Halide perovskites, particularly those containing lead such as $CsPbX_3$ (X=Cl, Br, I), have emerged as a new class of materials for applications in optoelectronics. However, the toxicity of lead necessitates the pursuit of lead-free alternatives. Bismuth-based halide double perovskite $Cs_2AgBiCl_6$ has emerged as a promising candidate, but there are still conflicting reports and interpretations regarding this material's optical properties, such as its bandgap and the origin of its characteristic high-intensity visible orange emission. Here, we report on synthesizing $Cs_2AgBiCl_6$ thin films through reactive thermal evaporation and address these discrepancies. Specifically, we deposited $Cs_2AgBiCl_6$ thin films by co-evaporating CsCl, $BiCl_3$, and AgCl onto glass substrates, which, upon reaction on the substrate, yielded polycrystalline thin films. Film thickness and stoichiometry were controlled by controlling the evaporation fluxes of the precursors using quartz crystal microbalances. Typical film thicknesses were 100-400 nm. Optical characterization analysis of the thin films reveals a bandgap of 2.77 eV. X-ray diffraction (XRD) and Raman spectroscopy were used to verify the phase purity and structure of the perovskite as well as impurity phases when present. Steady-state and time-resolved photoluminescence (TRPL) measurement of emission lifetime gave insights into the origin of the orange visible emission. We propose a mathematical model of emission kinetics considering both defect and self-trapped exciton emissions. The high-fidelity fitting of the data with only a few adjustable kinetic parameters suggests both defect and self-trapped exciton emissions may be present, and their contributions may depend on the synthesis conditions, possibly settling the debate in the literature. We also doped the $Cs_2AgBiCl_6$ perovskite with Yb by co-evaporating $YbCl_3$ during film deposition to explore the possibility of downconversion and quantum cutting, the generation of two near-infrared photons from one ultraviolet (UV) photon. The perovskite host absorbs the UV photon and transfers its energy to Yb, which then relaxes ($^2F_{5/2} \rightarrow ^2F_{7/2}$) and emits photons (1.25 eV) in the near-infrared. Doping with Yb resulted in a photoluminescence quantum yield (PLQY) of 50%, the highest reported in the literature for $Cs_2AgBiCl_6$. We investigated various post-deposition treatments, such as annealing in air versus in a nitrogen-filled environment, and concluded that annealing in air, in the presence of moisture, results in the formation of bismuth oxychloride (BiOCl), confirmed by XRD and Raman spectroscopy. We hypothesize that BiOCl passivates non-radiative defects, aiding in achieving high PLQY.

9:15am **TF1-MoM-5 Low-cost Grown a-Si:H Using Trisilane and its Application to Post Deposition Processes**, ***Benedikt Fischer**, M. Nuys, S. Haas, U. Rau,* Forschungszentrum Jülich GmbH, Germany

Hydrogenated amorphous silicon (a-Si:H) films are used in a wide range of semiconductor devices. Especially in the current highly efficient solar cell techniques named silicon heterojunction (SHJ) solar cells and tunnel oxide passivated contact (TopCon) solar cells, they are used directly as passivation layer or as a precursor for recrystallized silicon films, respectively. However, for the growth of the a-Si:H films, techniques like plasma enhanced chemical vapor deposition or electronic beam evaporation with expensive vacuum technology are used. Here we show a new setup for the deposition of a-Si:H by atmospheric pressure chemical vapor deposition using liquid trisilane allowing a fast and cost-effective deposition process. By varying the deposition temperature, time and precursor amount we could set the H-content of the films to $0 - 10\ \%_{vol}$ and achieved a maximum photosensitivity of 10^4 with a photconductivity of 10^{-7} S/cm. By applying post deposition H treatments, a photoconductivity of 5×10^{-6} S/cm could be achieved, leading to a photosensitivity of almost 10^5. The low H-content of the films allows annealing without blistering of the samples, especially for the films grown at a substrate temperature of ≥ 500°C. Therefore, we applied rapid thermal annealing to the films and achieved recrystallized silicon with conductivities up to 10^{-1} S/cm. The results show that the as deposited thermally grown films already have a high film quality, indicated by the high photosensitivity. The application of post H-treatment can further improve the film quality, approaching the photosensitivity of high quality PECVD films. Both photoconductivity and photosensitivity can be further increased by improving the hydrogenation process, which was not optimized yet. In addition, the high conductivity achieved by the rapid thermal annealing experiments in comparison with state-of-the-art films show the applicability in TopCon solar cells. Further investigations regarding film doping and application of the polysilicon films for the passivation in combination with a tunnel oxide are in progress. These results, and the fact that the films were produced by a low-cost deposition system, make them highly promising for an industrial application in solar cells.

9:30am **TF1-MoM-6 Optimization of DC Reactive Sputtering of NiOx Transport Layer and Effects of Annealing Conditions on NiOx film for Perovskite Solar Cells**, ***Firdos Ali**, S. Gupta,* University of Alabama

DC reactively sputtered NiO_x was optimized as a hole transport layer for perovskite solar cell applications. We introduced the reactively sputtered NiO_x hole transport layer over a spin-coated NiO_x layer in solution-processed perovskite (MeO-2PACZ/MAPBI3-XClx) solar cells. The typical reactive hysteresis effects were not observed on the cathode voltage while varying the reactive gas flow during deposition, and this case may be explained by Berg's hysteresis model. We have investigated the unusual hysteresis behavior of the cathode voltage as a function of oxygen flow rate in argon, and correlated this with the deposition rate. The NiOx films were infrared lamp annealed at various temperatures at high vacuum. Perovskite solar cells were fabricated using a solution processing method. A parallel set of devices were fabricated using hot-plate annealing of the NiO_x hole transport layer in atmosphere. The NiO_x thin films were structurally characterized using a variety of techniques: scanning electron microscopy (SEM), X-ray reflectivity (XRR), and X-ray diffraction. SEM studies were carried out to observe the surface morphology of the NiO_x film. A continuous film of NiO_x was observed at higher oxygen flows and lower deposition rates. XRD analysis on ITO/NiO_x thin films sputtered with various oxygen flows was carried out to study the crystal orientation and crystallinity. The effects of sputtered NiO_x deposition rate, film thickness, as well as annealing conditions on the solar cell efficiency were investigated. The power conversion efficiency was improved from 5% to 13.5 % .

9:45am **TF1-MoM-7 Optimizing Sputtered Nickel Oxides as Hole Transport Layers and Their Applications for Perovskite Solar Cells**, ***Jae Won Kim**, M. Kim, S. Lee,* Korea Research Institute of Chemical Technology (KRICT), Republic of Korea

Nickel oxide (NiO_x) has garnered attention as an efficient hole transport layer (HTL) in perovskite solar cells (PSCs) due to its wide bandgap, which effectively blocks electron transfer, a compatible work function that aligns well with the energy levels of perovskite (PVK) materials, and adequate carrier mobility. This study explores the significant impact of NiO_x layer thickness on the electrical characteristics and efficiency of PSCs. The NiOx layers were deposited using radio-frequency (RF) magnetron sputtering, a technique chosen for its capability to provide uniform thin films over large areas. By experimenting with NiO_x thicknesses ranging from 5 to 30 nm, it was determined that a 10 nm thick NiO_x layer yields the best performance.

Devices incorporating this optimal thickness demonstrated improved charge carrier extraction and transport properties, essential for achieving high-efficient PSCs. Photoluminescence (PL) and time-resolved photoluminescence (TRPL) measurements provide deeper insights into the charge dynamics within the PSCs. These analyses confirm that the 10 nm NiO_x layer facilitates a lower recombination rate and more efficient charge separation compared to thicker or thinner layers. Supporting these findings, transient photovoltage and photocurrent studies indicate faster charge extraction and prolonged carrier lifetimes, which contribute to higher power conversion efficiencies.

Moreover, energy band alignment investigations, including Hall measurement and ultraviolet spectroscopy, reveal that the 10 nm NiO_x layer optimizes charge transport from the perovskite layer to the HTL. The energy level offset between the valence band of NiO_x and PVK typically shows negative values, implying charge blocking at the interface; however, the 10 nm NiO_x layer displayed a minimal offset of 0.04 eV, resulting in efficient charge transport.

This paper significantly contributes to the field of photovoltaic research by highlighting the critical role of RF-sputtered NiO_x layer thickness in optimizing the performance of inverted PSCs. The findings suggest that precise control over the deposition of HTLs can lead to substantial improvements in PSCs efficiencies, offering a promising avenue for the development of more effective renewable energy technologies.

10:00am **TF1-MoM-8 Tunable Sn_xS_y Deposition onto Functionalized Alkanethiolate Self-Assembled Monolayers by Chemical Bath Deposition**, ***Christopher Brewer**, R. Woolard, T. Estrada, A. Walker,* University of Texas at Dallas

Tin sulfides (Sn_xS_y) are non-toxic and inexpensive materials with low band gaps, making them suitable for semiconductor applications and photovoltaic materials, such as solar cells.Sn_xS_y has three naturally occurring compositions, SnS, Sn_2S_3, and SnS_2, each with different properties.The ability to control the stoichiometry of a Sn_xS_y deposit is of interest for devices like SnS solar cells, where Sn_2S_3 contamination reduces the device efficiency.Chemical bath deposition (CBD) is a low cost and scalable technique that can be used under ambient conditions to deposit Sn_xS_y onto a variety of substrates, including organic substrates.Alkanethiolate self-assembled monolayers (SAMs), functionalized with $–CH_3$, –OH, and –COOH terminal groups, are a readily available system, which can be used as a model organic substrate for deposition of Sn_xS_y by CBD.A CBD bath has multiple tunable components, including the solution pH, complexing agent, bases used, and sulfur source as the most common.Modification of any of the bath components, as well as the SAM functionalization, can control the deposit's major composition and phase.Using a mechanism based approach, we have been able to tune the bath chemistry to yield pure SnS deposits.

Thin Films
Room 115 - Session TF2-MoM
Thin Films Special Session: Remembering Dr. Paul Holloway I

Moderators: Sean Jones, Argonne National Laboratory, **Robert Grubbs**, IMEC Belgium

10:30am **TF2-MoM-10 Fundamental Aspects of Focused Nanoscale Electron-Ion- and Photon-Beam Induced Processing and Recent Advances in Editing Transition Metal Dichalcogenide Materials and Devices**, ***Philip Rack**,* Department of Materials Science and Engineering, University of Tennessee, Knoxville **INVITED**

I graduated from Paul Hollloway's group at the University of Florida in 1997 where I studied luminescent materials for electroluminescent displays.If the saying is true that "imitation is the sincerest form of flattery," then my career path captures the admiration for the man I had the privilege to call my Phd advisor.In this talk, I will briefly discuss some of the luminescent materials research that my group has performed and overview my serendipitous journey to focused nanoscale electron beam induced processing, highlighting how it has been an eerily mirror image to Dr. Holloway's path. The scientific portion of my talk will review topics near and dear to Dr. Holloway's heart, electron(ion, photon)-gas-solid interactions, and illustrate that appropriate understanding of these interactions can result in directed growth/etching at the nanoscale.I will overview a Monte Carlo simulation we developed to illustrate some of the critical electron(ion, photon)-gas-solid interactions that can rate and resolution limit nanoscale focused beam induced processing.Finally, I will review our recent work in focused electron beam induced etching of MoS_2 multi- and single-layer devices.

11:00am **TF2-MoM-12 Stability of Phosphor Thin Films During Cathodoluminescence and Upconversion**, ***Hendrik Swart**,* University of the Free State, South Africa **INVITED**

Surface characterization and optical characterization techniques play a vital role in the complete understanding of the luminescent properties of phosphor nanomaterials and thin films. Auger electron spectroscopy (AES), X-ray photo electron spectroscopy (XPS), time of flight scanning ion mass spectrometry (TOF SIMS), Photoluminescence (PL) and cathodoluminescence (CL) are used to characterize these different phosphor materials and thin films. The crystal field that is determined by the environment in the host material in combination with the various dopant ions with the correct valence state can be used to obtain emissions from the Ultraviolet (UV) to the infra-red (IR) wavelength ranges. Phosphor materials have been successfully used to improve the efficiency of various applications. Nanoparticles both undoped and doped with different rare earth elements were synthesized by several synthesized techniques. The defects incorporated into the bulk material play an important role in the emission efficiency and colour scheme. XPS in combination with PL can be used to identify some of these defects in the material. Thin films of different phosphors have been deposited using the Pulsed laser deposition (PLD) and spin coating techniques. Degradation of the different phosphors during prolonged electron/photon bombardment also played a vital role in their possible applications. The combination of CL, PL, AES and XPS techniques helps to determine the mechanisms behind the degradation. A small number of impurities in the chemicals used during synthesis can play a large role in the final emission intensity and colour of the phosphor materials. TOF SIMS can point out these impurities. It is also important to test the suitability of phosphors powders and thin films during prolonged upconversion photoluminescence. Examples of different phosphor materials with different applications such as Solid-State Lighting will be shown.

11:30am **TF2-MoM-14 Extracting Diffusing Parameters for Indium Segregating form Copper using TOF-SIMS***, **Jacobus Johannes Terblans**, L. Makoloane, S. Cronje, H. Swart,* University of the Free State, South Africa

Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS), with its superior concentration detection limit (in the parts per million (ppm) range) and its ability to operate in static mode (where only the top 1-2 monolayers contribute to the measuring signal), makes TOF-SIMS a technique that is widely used for surface characterisation. This makes TOF-SIMS particularly suitable for studying surface segregation.However, concentration calculations are significantly influenced by the matrix effect, which makes it difficult to perform quantitative measurements.To investigate the segregation of indium with TOF-SIMS, the concentration quantification was addressed by utilising a set of Cu/In thin films of varying concentrations to calibrate the TOF-SIMS system by determining the In sensitivity factor relative to a Cu matrix. The Cu/In thin films used for the calibration were prepared using the Electron Beam Physical Vapor Deposition (EBPVD) co-evaporation method, and the composition of the films was controlled by varying the deposition rates of In and Cu.

To study indium segregation from copper, a polycrystalline Cu crystal was doped with 0.5 at% In by evaporating In onto a polycrystalline Cu crystal and annealing it at 1173 K for 23 days. Indium segregation was stimulated by heating the In-doped polycrystalline Cu crystal linearly from 323 K to 873 K with a heating rate of 0.1 K/s.At the same time, the surface concentration of In was recorded with TOF-SIMS as a function of temperature.The recorded segregation profile was fitted with the modified Fick semi-infinite, the Langmuir-McLean, and modified Darken models.The semi-infinite Fick model successfully extracted the pre-exponential factor (D_0) and activation energy (Q) of 1.44×10^{-5} m^2s^{-1} and 183.3 kJ/mol, respectively, from the kinetic region of the segregation data.With the Langmuir-McLean model, fitted to the equilibrium region, a segregation energy of -64.6 kJ/mol was obtained.The modified Darken model was fitted to the segregation profile, and the segregation parameters were determined as $D_0 = 0.50 \times 10^{-5}$ m^2s^{-1}, Q = 176.0 kJ/mol, and $\Delta G = -64.4$ kJ/mol.These diffusion parameters were in good agreement with the segregation parameters obtained using Auger electron spectroscopy measurements.

11:45am **TF2-MoM-15 Commercializing Nanowire LEDs***, **David Laleyan**, B. Le, G. Frolov,* NS Nanotech Canada*; M. Stevenson, S. Coe-Sullivan,* NS Nanotech

MicroLED display technology consists of many carefully arranged microscopic light-emitting diodes (LEDs) to directly create color pixels. MicroLED displays thus have the potential brightness, efficiency, and response time of inorganic LEDs, but suffer from the high cost of epitaxy, as well as the challenges of creating red, green, and blue materials on a single material and substrate. Furthermore, conventional approaches of growing planar LEDs and then etching them into micron scale devices causes a fundamental loss of efficiency, especially for the smallest devices. In this regard, nanowire-based LEDs for microLED applications have been of great interest and a topic of extensive research for over a decade. This is due to their unique ability to maintain high efficiencies even as the LED size becomes quite small, even into the sub-micron regime, contrary to conventional thin-film LEDs. Another valuable benefit is the ability to form photonic crystal arrangements, such that the formation of a photonic bandgap leads to highly directional and narrow bandwidth emission. More recently, reports have shown nanowire LEDs in the green with >25% external quantum efficiency (EQE) and red with >8% EQE, competitive with the best direct green and InGaN red LEDs ever fabricated – despite being sub-micron in size. These structures were obtained by molecular beam epitaxy (MBE) using a selective area epitaxy (SAE) technique, where nanostructures can be controllably grown on a thin-film template. Novel development and engineering efforts are required for such nanowire LEDs to become commercially viable. This work presents a pathway towards the wafer-scale production of nanowire LEDs for displays. This talk will explain how breakthrough academic research can be made manufacturable by studying run-to-run variability, understanding the process windows, targeting yield-limiting steps, and ensuring process scalability. Focusing on the reproducibility and uniformity of nanowire growth by SAE is the first critical step toward the large-scale deployment of these highly efficient LED that are perfectly suited for the next generation of microLED displays.

Atomic Scale Processing Mini-Symposium
Room 116 - Session AP1+EM+PS+TF-MoA

Area Selective Deposition (ASD) II

Moderators: Satoshi Hamaguchi, Osaka University, Japan, **Greg Parsons**, North Carolina State 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 iskey in successfully realizing defect free area selective deposition. Surface sensitive and reaction driven processes such 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 MgF2 window and UV photons are focused onto the sample using a convex MgF2 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_2 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_2 and Al_2O3 capping layers on Cu with respect to polymers are studied and their reliability performance investigated

3:30pm **AP1+EM+PS+TF-MoA-9 SiO_2 Fluorination/Passivation for Area-Selective Deposition of TiO_2, ZnO, and Polymer on Metal and SiN_x vs. SiO_2***, **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_2O_3, ZnO, and TiO_2) on hydroxylated and fluorinated SiO_2, and hydroxylated and fluorinated silicon nitride, SiNx, 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_2 and SiNx in electronic device processing, and because of the chemical similarity of these surfaces. To explore ASD on SiNx and SiO_2, we exposed blanket SiNx and SiO_2 wafers to multiple doses of molybdenum hexafluoride, MoF_6, at low temperature (~200°C). Based on XPS analysis, the MoF_6 exposure leads to fluorination of both surfaces. Then, we performed polypyrrole (PPy) oxidative-CVD using pyrrole monomer and $SbCl_5$ 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 SiNx surface after some nucleation delay, but on SiO_2, only isolated nuclei were formed. Control experiments using SiNx and SiO_2 substrates without the MoF_6 exposure step showed uniform deposition on both substrates. To extend this demonstration of ASD of SiNx vs SiO_2 to other materials and substrates, we tested ALD of TiO_2, ZnO, and Al_2O_3 SiO_2, SiNx and Mo metal after exposure to MoF_6. We find that this selective fluorination passivation of the SiO_2 surface allows for selective growth of TiO_2 and ZnO on Mo vs SiO_2, whereas ALD Al_2O_3 using TMA/H_2O showed uniform, non-selective deposition. Moreover, after exposing SiO_2 and SiNx to MoF_6, TiO_2 ALD using $TiCl_4$/H_2O deposited on SiNx after some delay, whereas a much longer delay was observed on SiO_2. 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_2, SiNx and metal after exposure to MoF_6 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

Moderators: Satoshi Hamaguchi, Osaka University, Japan, **Greg Parsons**, North Carolina State University

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.[1] 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.[2]

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:

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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_2/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_2, 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_2 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_2, H_2, and NH_3 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.

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_2Cl_2 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_2 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.

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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.[1] 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_2O_3 surface in chelate and monodentate adsorption configurations.[2] 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. Merkx *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.

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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 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 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 µm 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.

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8:30am **2D+AP+EM+QS+SS+TF-TuM-3 High-Coverage MoS_2 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_2 on SiO_2/Si substrate. The process starts with growing an initial film on SiO_2/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_{2g} and A_{1g} peaks are observed in entire substrate which shows that MoS_2 is grown with high coverage. The difference of E_{2g} and A_{1g} peaks is about 21 cm^{-1}. These results indicate that the two-step annealing process is suitable for obtaining MoS_2 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. Puretzky, 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 MoS2, 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 MoS2. 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 MoS2resulted 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. Krasheninnikov,* 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 $MoSe_2$ 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.

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9:15am **2D+AP+EM+QS+SS+TF-TuM-6 Location-Selective CVD Synthesis of Circular MoS_2 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 MoS2 as an example, we develop a precursor-seeded growth strategy for the direct and site-specific synthesis on SiO2 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 MoS2 flakes are successfully grown with the MoO3 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 MoS2 flakes. The tri-layer circular MoS2 arrays possess an adjustable and uniform size and exhibit a consistent field-effect mobility up to ~20 cm2/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_2/WS_2 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_2/WS_2) on various substrates (such as sapphire and SiO_2/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. Puretzky, I. Vlassiouk, 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 know layered materials, such as $PtTe_2$ +Pt => Pt_2Te_2 [1], new phases such as mirror twin grain boundary networks in $MoSe_2$ or $MoTe_2$ [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.

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Post-Synthesis Modifications of Two-Dimensional MoSe2 or MoTe2 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 PtTe2 to Pt2Te2.

Nano Letters 22, 9571-9577 (2022)

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2D Materials by Design: Intercalation of Cr or Mn between two VSe2 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 Bi_2Se_3 and transform the surface layer into XBi_2Se_4 (X = 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 Bi_2Se_3 is reduced to Bi_2-layer, and a stable (pseudo) 2D $Cr_{1+\delta}Se_2$ layer is formed, whereas $MnBi_2Se_4$ phase is formed with a mild annealing for monolayer amount of Mn deposition.[1] 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.[1] The success of obtaining the $MnBi_2Se_4$ septuple layer manifests a promising approach for engineering other multicomponent vdW materials by surface reactions.

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[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 Award Finalist Talk: Quasi-Van Der Waals Epitaxial Growth of Thin γ'-Gase Films**, ***Mingyu Yu***[1]*,* 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 650-180000nm, 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: ε-(2H), β-(2R), δ-(4H), and γ-(3R). They have identical non-centrosymmetric QL with a D_{3h} space group. Besides the four extensively explored polymorphs, a new polymorph, γ'-(3-R) GaSe, was proposed for the first time in 2018. γ'-GaSe is unique for its centrosymmetric D_{3d} QL (Fig. S1), for which γ'-GaSe is predicted to show intriguing properties compared to other polymorphs. However, there are few existing reports on the observation of γ'-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 γ'-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 γ'-polymorph using scanning transmission electron microscopy (Fig. S2c,d). Through density-functional theory analysis (Fig. S3), γ'-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, γ'-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 γ'-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 γ'-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 Hajzus****, 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 SiO_2/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√3 buffer layer that forms during growth on SiC(0001) remains on the SiC substrate. Consequently, if there are regions of exposed 6√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√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.

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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 Si_3N_4 and SiO_2 films using the formation and desorption of $(NH_4)_2SiF_6$-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

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[1] **AVS National Student Award Finalist**

modified layers, enabling conformal and precisely controlled etching. In addition, spontaneous and highly selective etching of SiO_2 was demonstrated on the DCR tools using HF/CH_3OH vapor. SiO_2 films can be etched spontaneously with high selectivity to SiN films when the temperature of the substrate is lower than −20ºC.

8:30am **AP1+EM+PS+TF-TuM-3 Selective Si or Ge Dry, Thermal Spontaneous Etching Using HF Vapor***, **Marcel Junige**, T. Colleran, 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℃. The Si etch rate was 12.2 Å/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 SiO_2 and stoichiometric Si_3N_4.

Temperature-programmed quadrupole mass spectrometry (QMS) experiments confirmed the spontaneous etching of crystalline Si nano-powder by HF. SiF_4 and H_2 were observed as the main volatile etch products. QMS detected the SiF_4 product with a gradual onset above ~175℃. This temperature dependency indicated that the etch reaction may be limited by SiF_4 desorption from the Si surface. SiF_4 desorption from fluorinated Si surfaces has been reported to occur at >125℃.

Additional QMS experiments also observed the spontaneous etching of Ge nano-powder by HF. GeF_4 and H_2 were revealed as the main volatile etch products. QMS detected GeF_4 already at 25℃. The GeF_3^+ signal intensity increased with elevating temperature and exhibited a maximum at ~80-85℃. Subsequently, the GeF_3^+ signal decreased below the noise level above ~125℃.

These results suggest that Si etching could be achieved selectively over Ge retention at >175℃. Likewise, Ge etching could be accomplished selectively over Si retention at <125℃. 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 SO_2Cl_2 for halogenation and $P(CH_3)_3$ 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.

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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 µLEDs 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 µLEDs. 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 µLED 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 0.5–1.0 Å/cycle at temperatures from 300–330 °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 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 XPS 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 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 ~4 nm.

9:15am **AP1+EM+PS+TF-TuM-6 Temperature-Dependent Atomic Layer Etching of Polycrystalline, Epitaxial, and Doped ZnO Films: An *in situ* Spectroscopic Ellipsometry Investigation***, **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.

In this work, we apply ALE to zinc oxide (ZnO) films, focusing on the influence of the film's structure (i.e., crystallinity and doping) on the etch rates. Utilizing *in situ* spectroscopic ellipsometry, we comprehensively map the etch rate as a function of temperature and pulse times for the reactants. The resulting 3D contour plot of etch rate vs.temperature and pulse time defines the process parameter 'window'. Notably, this plot is visually captivating and aids in the comprehension and optimization of the ALE process.

The ALE process employed for ZnO etching consists of alternate pulses of acetylacetone and O_2 plasma, spanning temperatures from 120 °C to 300 °C.[1]The etch rates of epitaxial, single crystalline films are compared with polycrystalline ZnO. The effect of dopants, such as Al^{3+}on the etch rates of ZnO films are explored. The impact of ALE chemistry in determining etch rates in films with crystal facets, grain boundaries and dopants are discussed with implications to future device manufacturing.

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9:30am **AP1+EM+PS+TF-TuM-7 Examination of Atomic Layer Etch Mechanisms by Nuclear Magnetic Resonance Spectroscopy***, T. Smith, **Jane P. 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[1]. 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 $Cu(HCOO)_2 \cdot 4H_2O$ as a product is possible by comparison to a commercial reference powder. However, assignment of other peaks requires correlation spectroscopy showing ^{13}C-^{13}C and ^{1}H-^{13}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 (LiNbO3, 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_2 and SF_6/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_6/O_2 or Cl_2/BCl_3 plasma exposures in place of the SF_6/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+ 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_2O_3 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_2O_3 is an ultra-wide band gap material with important applications for high power electronics. High precision etching is required for β-Ga_2O_3 device fabrication. Previous thermal atomic layer etching (ALE) attempts to etch β-Ga_2O_3 have not been successful. Plasma etching of β-Ga_2O_3 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_2O_3 is performed using a HCl reactive background gas (RBG) and positive sample bias. The β-Ga_2O_3 is a -oriented epitaxial film grown by suboxide molecular-beam epitaxy on a single-crystal (0001) Al_2O_3 substrate. The ~100 eV primary electrons from a hollow cathode plasma electron source (HC-PES) are incident on the β-Ga_2O_3 sample. The HC-PES is a chemically robust electron source capable of delivering >200 mA over an area >10 cm^2. 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_2O_3 film thicknesswas monitored using in situ spectroscopic ellipsometry during electron exposure. Figure 1 shows that the etching of β-Ga_2O_3 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^- through dissociative electron attachment ionization. (4) The Cl^- negative ions are attracted to the sample by the positive sample stage voltage. (5) The incoming Cl^- 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_2O_3 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_2O_3 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.

11:45am **AP2+EM+PS+TF-TuM-16 Bias-Pulsed Atomic Layer Etching***, **Julian Michaels**,* University of Illinois at Urbana-Champaign*; N. Delegan,* 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_6 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_6 followed by Ar^+ 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_6 under Ar^+ ion bombardment where further sputtering does not occur once all of the adsorbed SF_6 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)

Thin Films
Room 115 - Session TF1-TuM

Thin Films: Controlling Crystalline Phases

Moderators: Lauren Garten, Georgia Institute of Technology, **April Jewell**, Jet Propulsion Laboratory

8:00am **TF1-TuM-1 Peter Mark Memorial Award Talk: Strain-Induced Magnetism and Superconductivity in Single-Crystalline Heusler Membranes*, Jason Kawasaki*[1]**, University of Wisconsin - Madison **INVITED**

Single-crystalline membranes of functional materials enable the tuning of properties via extreme strain states; however, conventional routes for producing membranes require the use of sacrificial layers and chemical etchants, which can both damage the membrane and limit the ability to make them ultrathin. I will describe how the growth of thin films on graphene-terminated substrates enables synthesis of single crystalline, mechanically exfoliatable membranes [1,2]. Using rippled membranes of the Heusler compound GdPtSb, we demonstrate the first experimental example of flexomagnetism, that is, ferro/ferri-magnetism induced by strain gradients [3]. I will also describe evidence of superconductivity induced in another Heusler membrane via strain. More broadly, Heusler membranes provide highly tunable platform for tuning ferroic order, topological states, and correlations [4].

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8:30am **TF1-TuM-3 Stabilization of P63cm $ScFeO_3$ on (111) Pt Mediated via an Fe_3O_4 Interlayer*, Marshall Frye,*** *J. Chin,* Georgia Institute of Technology*; N. Parker, M. Barone,* Cornell University*; L. Garten,* Georgia Institute of Technology

Marshall Frye1, Jonathan Chin1, Nicholas Parker2, Matthew Barone3, Lauren M. Garten1

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Ferroelectric photovoltaics are an emerging renewable energy technology where charge separation occurs in a single layer and the open-circuit voltage can be larger than the bandgap. The metastable $P6_3cm$ phase of $ScFeO_3$ (h-$ScFeO_3$) is an ideal candidate for ferroelectric photovoltaics due to its polar crystal structure and narrow bandgap (1.2 eV). While h-$ScFeO_3$ can be grown on Al_2O_3 using a layered approach,[1] on conductive substrates, such as (111) Pt, only the ground state bixbyite phase of $ScFeO_3$ is stable. h-$ScFeO_3$ growth on a substrate with high conductivity and low epitaxial strain is critically needed for photovoltaic device fabrication.

In this work we grew h-$ScFeO_3$ on (111) platinum via molecular beam epitaxy (MBE). The stabilization of the h-$ScFeO_3$ phase was enabled by an Fe_3O_4 interlayer. This approach is adapted from reports of growth of hexagonal $LuFeO_3$ on oriented Fe_3O_4 via MBE.[2] Epitaxial (111) Pt which was deposited on c-Al_2O_3 was found to have a narrow (~0.005°) full width at half maximum (FWHM) rocking curve about the (111) peak, indicating a highly crystalline film. After depositing (111) Pt, a Fe_3O_4 layer was deposited. $ScFeO_3$ was then deposited on the Fe_3O_4 film with alternating depositions of Sc and Fe.[1] The films are solely (000*2l*) oriented of h-$ScFeO_3$ with clear Laue oscillations. Furthermore, rocking curves about the (0004) hexagonal $ScFeO_3$ peak have a FWHM of 0.07°, indicating a highly crystalline film. Films grown on conductive substrates then enabled measurements of the carrier mobility and dielectric response of the h-$ScFeO_3$. Overcoming the challenge of growing h-$ScFeO_3$ on conductive substrates will allow us to utilize these materials advantageous properties for high-efficiency photovoltaics.

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1. Zhang, X. *et al.* Effect of interface on epitaxy and magnetism in h-$RFeO_3/Fe_3O_4/Al_2O_3$ films (R = Lu, Yb). *J. Phys. Condens. Matter* **29**, 164001 (2017).

8:45am **TF1-TuM-4 Thermo-Controlled Defect Engineering in Ceria: An XPS and Raman Spectroscopy Study with In-Situ Heating***, U. Kumar, C. Feit, J. Prakash Ganesan, S. Berriel, Y. Fu, C. Neal, E. Kolanthai, P. Banerjee,* ***Sudipta Seal,*** University of Central Florida

Cerium oxide nanostructures possess unique oxidative recycling properties, enabling their use in various engineering applications. However, predictable and precise defect engineering remains challenging. Ceria thin films offer a method to engineer defects by controlling thickness, albeit with limitations. To further enhance performance, we fabricated 2.9 nm and 0.5 nm CeO2-33 nm VO2 bilayers using atomic layer deposition (ALD), leveraging the low-temperature phase transition of VO2. We established a test vehicle utilizing X-ray Photoelectron Spectroscopy (XPS) with in-situ heating and cooling to study defect levels. The Ce3+/Ce4+ ratio was determined using Ce3d XPS scans during heating and cooling. A remarkable Ce3+/Ce4+ ratio of 5.97 (Ce3+ ~ 85%) was obtained and modulated over a temperature range from room temperature to 90 ÂºC. Additionally, Raman studies with in-situ heating and cooling were conducted to understand the mechanism behind this phenomenon.

9:00am **TF1-TuM-5 Hybrid Pulsed Laser Deposition Growth of Epitaxial Chalcogenides*, Mythili Surendran,*** USC

Chalcogenides such as transition metal dichalcogenides (TMDC) and chalcogenide perovskites (CP) have garnered attention for their electronic and photonic properties. Despite their promising potential for electronic applications, the epitaxial growth of these materials is still in its nascent stages. Adding to the complexity, a most of the emerging chalcogenides are vapor pressure mismatched transition metal compounds. The stark differences in vapor pressures between transition metal cations and chalcogen anions present a great challenge during epitaxial growth. This challenge is particularly pronounced in sulfide thin film growth and exacerbated in CPs due to their complex stoichiometries. Addressing these complexities demands innovative strategies to achieve precise flux control and maintain stoichiometric integrity during epitaxial growth.

Sulfides have been mostly grown using CVD, although MBE, MOCVD, pulsed laser deposition (PLD)and several other techniques have been exploited. However, large area and high-quality growth with precise and uniform thickness control and low defect densities still remain a challenge due to a large cation-sulfur vapor pressure mismatch, corrosive and reactive nature of most chalcogen precursors, high synthesis temperatures and the propensity to oxidize easily in the presence of oxygen at these high temperatures. Most growth techniques utilize H2S as the sulfur source.

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[1] **Peter Mark Memorial Award Winner**

However, H_2S is a toxic, hazardous, and flammable gas and require high temperatures for efficient decomposition and sulfurization, resulting in high defect densities.

Here, we discuss epitaxial growth of CPs and TMDCs (specifically sulfides) using a novel hybrid PLD (*Adv. Mater* 2024) approach wherein we employed organo-sulfur precursors as the sulfur source. Large area epitaxial thin films of Group IV 2D chalcogenides such as TiS_2 (metallic) and ZrS_2 (semiconducting) and CPs such as $BaZrS_3$ and $BaTiS_3$ were successfully grown. This novel method utilizes precursors with optimum vapor pressures and they decompose at a lower temperatures (~250-400°C) to provide dissociated sulfur species. Structural and electrical characterization, along with low temperature transport studies reveal low defect densities and high carrier mobilities in these films. This work emphasizes on low temperature growth of high mobility refractory metal-based sulfides, especially with BEOL compatibility. Although slightly elevated temperatures were required for CPs, the interfacial roughness and optoelectronic performance were improved. The potential of these chalcogenides as candidates for transparent and conducting layers in chalcogenide-based optoelectronic devices will be discussed.

9:15am **TF1-TuM-6 Atomic Layer Deposition of Entropy Stabilized Zr_xTa_yOz**, ***Shane Witsell**, J. Haglund, J. Conley,* Oregon State University

High entropy oxides (HEOs) can exhibit enhanced mechanical, refractory, catalytic, cryogenic, and dielectric properties over conventional materials [1]. The classic understanding of HEOs is founded on a high degree of configurational disorder as well as a positive enthalpy of formation. It has been thought that five discrete elements were necessary to cause this high degree of disorder (S_{config} >1.6R,J/mol*K*)*. However, it has recently been shown that $A_6B_2O_{17}$ perovskites, where A = Zr or Hf and B = Nb or Ta can demonstrate an exceptionally high degree of disorder (S_{config} of 4.50R, J/mol*K) [2]. Though these materials have been synthesized by powder sintering [5] and ternary ZrTaO has been demonstrated with atomic layer deposition (ALD) [3], entropy stabilized $Zr_xTa_yO_z$ has yet to be achieved via ALD. Herein we report the successful transformation of ALD $Zr_xTa_yO_z$ into the entropy-stabilized form.

ZrO_2 and Ta_2O_5 were synthesized via ALD using tantalum ethoxide ($Ta(OEt)_5$) and zirconium chloride ($ZrCl_4$), respectively, with O_3 [3]. $Zr_xTa_yO_z$ was deposited using modulated $ZrCl_4/N_2/Ta(OEt)_5/N_2/O_3/N_2$ super cycles [4]. Films were deposited on Si substrates and were amorphous as-deposited. Following annealing at 800°C for 30 minutes in N_2, x-ray diffractometry (XRD) spectra (Fig. 1) show a strong overlap between annealed ALD $Zr_6Ta_2O_{17}$ and the expected peaks for HEO stabilized $A_6B_2O_{17}$ [5], and no overlap with binary ZrO_2 or Ta_2O_5.

Metal/insulator/Si (MIS) electrical devices were fabricated using Ag top electrodes. 800 °C annealed entropy stabilized $Zr_xTa_yO_z$ devices exhibited unipolar threshold voltage switching when illuminated, with a ON/OFF current ratio of $7x10^3$ and a ~ +0.56 MV/cm SET voltage. Switching did not occur in the dark. Unannealed amorphous $Zr_xTa_yO_z$ devices did not exhibit switching in this voltage range but required a +1.8 MV/cm SET voltage and had an ON/OFF ration of only $\sim 10^2$. Switching under illumination is still under investigation and was possibly due to the formation of oxygen vacancies in the entropy stabilized matrix as opposed to the un-annealed amorphous form [6].

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9:30am **TF1-TuM-7 Stabilizing Oriented Barium Nickelate Thin Films**, ***Ian Graham**, M. Frye, L. Garten,* Georgia Institute of Technology

Oxygen evolution reaction (OER) is the rate limiting step inhibiting the production of fuel from water.[1,2] Barium nickelate ($BaNiO_3$) is a potential candidate for OER catalysis because it has an order of magnitude higher catalytic activity for the OER compared to the current benchmark iridium oxide (IrO_2).[1] Understanding the impact of crystallographic orientation and oxygen vacancy concentration on OER catalytic activity is critical to enabling $BaNiO_3$ catalysts. [1,2]

In this work, we demonstrate the growth of oriented $BaNiO_3$ films via pulsed laser deposition (PLD). Films were deposited from a $BaNiO_{2.36}$ target onto (0001) Al_2O_3 substrates over a range of deposition temperatures, laser fluences, and oxygen partial pressures. X-ray diffraction shows that the orientation of $BaNiO_3$ is dependent on the deposition temperature. The (11-20) orientation of $BaNiO_3$ grows at temperatures below 500 °C, whereas increasing the deposition temperature from 400 °C to 500 °C leads to (10-10) $BaNiO_3$. Further increasing the deposition temperature to 700 °C changes the orientation of the film to predominately (0002) oriented. X-ray photoelectron spectroscopy shows the oxidation state of films deposited under different deposition oxygen partial pressures. Reducing deposition pO_2 from 1.65 x 10^{-2} mbar to 1.27 x 10^{-2} mbar shows a 4% decrease in oxygen atomic percentage. Atomic force microscopy shows that decreasing the laser fluence and oxygen partial pressure decreases the root mean square surface roughness of the deposited films. Reducing the laser fluence from 3.5 J/cm^2 to 2.5 J/cm^2 shows a 3 nm decrease in the root mean square surface roughness, while decreasing the oxygen partial pressure from 9.1 x 10^{-2} mbar to 1.65 x 10^{-2} mbar shows a 1 nm decrease in root mean square surface roughness. Co-planar top electrodes enabled impedance spectroscopy and dielectric measurements. Impedance data shows the migration of oxygen vacancies which play an important role in OER. Elucidating the impact of crystallographic orientation on oxygen vacancy migration gives insight into how crystallographic orientation affects OER catalytic activity.

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9:45am **TF1-TuM-8 Optimizing Sputter Deposition of Bi_2Te_3 and Sb_2Te_3 for Photolithographic Device Fabrication**, ***Rumana Zahir,*** University of Central Florida*; F. Gonzalez,* Truventic LLC*; D. Smalley, A. Bharath, E. Nino, K. Sundaram, M. Ishigami, R. Peale,* University of Central Fllorida

Antenna-coupled thermoelectric junctions have potential for THz and mm-wave detection and energy harvesting. These require patterned deposition of thermoelectric materials with a junction at the feed of a suitable antenna, where the junction is heated by the received radiation. Sb_2Te_3 and Bi_2Te_3 thin films have ideal thermoelectric properties for this application, and deposition over patterned photoresist on suitable substrate followed by lift-off is the simplest patterning approach. Our optimization study of unpatterned sputtered films on heated substrates required temperatures exceeding 175 °C to obtain ideal thermoelectric performance. Such temperatures tend to carbonize photoresists, complicating the subsequent lift-off. Here we report the results of a new optimization study using lower substrate temperatures during sputtering followed by annealing. Our approach considers three factors in a two-level full factorial optimization experiment. The three factors are substrate temperature during sputtering, subsequent vacuum annealing temperature, and annealing time. High and low values are selected for each factor giving 8 possible combinations. A mid-point tests for curvature in the main effects. The nine depositions per material were performed on glass substrates in randomized order. Graphs of the response (Seebeck coefficient) averaged over two of the factors plotted vs the third reveal the main effects of varying each factor. Graphs of the response averaged over one of the factors and plotted vs a second factor for each value of the third factor reveal interactions between factors. Examples of device fabrication following the optimized recipe, characterization, and simulation will be presented.

Thin Films

Room 115 - Session TF2-TuM

Thin Films for Extreme Environments

Moderators: April Jewell, Jet Propulsion Laboratory, **Lauren Garten**, Georgia Institute of Technology

11:00am **TF2-TuM-13 Nanoscale Metasurfaces for UV Spectropolarimetric Applications**, ***Tobias Wenger**, D. Nemchick, D. Wilson, R. Muller, K. Manatt, F. Winiberg, W. Johnson,* Jet Propulsion Laboratory (NASA/JPL)*; H. Hsiao,* National Taiwan University, Taiwan*; B. Drouin,* Jet Propulsion Laboratory (NASA/JPL) **INVITED**

In this talk I will describe our efforts to develop optical metasurfaces for applications in the ultraviolet part of the spectrum. Metasurfaces are made from subwavelength elements that can be thought of as imprinting a phase on incident wavefronts, thereby allowing precise control over light by use of micro-fabrication methods. Here, I will focus on our work on UV spectropolarimetric gratings intended for vertical ozone profiling within Earth's planetary boundary layer. Particular emphasis will be on the fabrication of metasurface nanostructures with high aspect ratios and feature sizes well below 100 nm. To accomplish this, we utilize low-temperature atomic layer deposition on resist preform structures fabricated using electron-beam lithography. To date we have used this method to fabricate metasurfaces from a variety of materials, e.g., hafnium oxide.

11:30am **TF2-TuM-15 Amorphous Boron Carbide-Amorphous Silicon Heterojunction Devices for Neutron Voltaic Application***, **Vojislav Medic**, N. Ianno,* University of Nebraska - Lincoln

Amorphous hydrogenated boron carbide (a-BC:H) has been extensively researched as a semiconductor for neutron voltaic device fabrication. Previous work on a-BC:H devices investigated the fabrication of homojunction, heterojunction and heteroisomeric devices from the polymeric precursors ortho-carborane (p-type) and meta-carborane (n-type) using plasma enhanced chemical vapor deposition (PECVD).

The p-type single crystal silicon (c-Si) with n-type a-BC:H grown from meta-carborane has been previously studied and shown to produce the most optimal device performance compared to different a-BC:H device structures (Figure 1). However, as c-Si degrades over time due to radiation induced damage to its crystalline structure, p+ type hydrogenated amorphous silicon (a-Si:H) was identified as a viable layer for development of the a-BC:H heterojunction device.

Characterization via 4-wire current-voltage measurements, X-ray Photoelectron Spectroscopy (XPS) and ellipsometry of a-BC:H/c-Si and a-BC:H/a-Si:H devices was done, and the a-BC:H/a-Si:H device shows potential in fabricating a novel neutron voltaic device. Utilizing well known material and electronic properties of c-Si, Kraut's method for calculating valence band offset (VBO) at the interface junction via XPS (Equation 1) was used to produce a band structure of both c-Si/a-BC:H and a-Si:H/a-BC:H p-n heterojunction devices (Figures 2-5).

Equation 1: $VBO = \Delta E_v = (CL\text{-}VBM)_{Si} - (CL\text{-}VBM)_{BC} + (CL_{BC}\text{-}CL_{Si})_{int}$

Additionally, the metal contact formation with a-BC:H has not been previously studied with respect to its possible effects on device performance. The metal/a-BC:H contact investigation was performed, identifying Ti as an Ohmic contact with n-type a-BC:H (Figure 3).

11:45am **TF2-TuM-16 Investigating the Practical Limits of Delta Doping by Low-temperature Silicon Molecular Beam Epitaxy***, **April Jewell**, M. Hoenk,* Jet Propulsion Laboratory

Silicon-based photodetectors and imaging arrays are used in nearly every space-based mission, including those for astrophysics, heliophysics, planetary science, and Earth science. In order to achieve the highest sensitivity and stability, silicon detectors must be properly passivated; JPL's approach to surface passivation uses low-temperature molecular beam epitaxy (MBE) to embed an atomically thin (i.e. <monolayer) delta layer of dopant atoms with nanometers of the silicon surface. The delta doping process allows for nanometer-scale control of the near surface band structure, which can be fine-tuned through dopant concentration, number of delta layers, layer separation, and depth. Most scientific silicon imaging arrays—including charge coupled devices (CCDs) and complementary metal oxide semiconductor (CMOS) image sensors—are backside illuminated to maximize efficiency, and the delta-doped layers are deposited on the back surface. In all of JPL's work on development and deployment of delta-doped detectors, our fabrication process has required heating the substrate surface to at least 400 °C to prepare the hydrogen-terminated surface for epitaxial growth. However, the same hydrogen chemistry that enables epitaxial growth can also lead to depassivation of the Si-SiO_2 interface in frontside MOS gate structures; furthermore, the 400°C temperature may result in thermal stresses at the interfaces or through-silicon-vias in 3D stacked detectors. Here we report on recent work to investigate the practical limits of low temperature MBE in an effort reduce the minimum substrate temperature required to achieve epitaxial growth and good dopant activation in delta-doped detectors.

12:00pm **TF2-TuM-17 Improvement of Coating Uniformity on Non-Planar, Non-Stationary Substrates Through a Combined Experiment-Simulation Approach***, **Sean Hayes**, S. Baxamusa, J. Biener, X. Lepro-Chavez, J. Forien, T. Parham, T. Braun, L. Sohngen,* Lawrence Livermore National Laboratory*; C. Wild, T. Fehrenbach,* Diamond Materials GmbH, Germany

Laser inertial confinement fusion (ICF) has come into worldwide focus after the historic experiment on December 4th, 2022 which achieved a target gain >1 for the first time at the National Ignition Facility.ICF experiments on NIF utilize ultrathick(~80-95μm) hollow spherical CVD diamond capsules that must have a coating with >99.8% thickness uniformity to efficiently convert laser energy to compression energy. The CVD diamond is coated on a spherical substrate that is agitated during deposition to ensure even coating. This work provides a framework for understanding the combined effects of instantaneous coating non-uniformity (ICNU) and substrate reorientation on coating uniformity.ICNU measurements on characteristic ensembles of shells in controlled settings were used to understand the effect of the number of nearest neighbors (coordination number, CN). These measurements were used as inputs for Monte Carlo simulations and tested against dynamic batch coatings to determine the effects of CN and FWHM of overall coating non-uniformity, and to infer reorientation times. Such an approach allows us to connect physical processes and dynamics to coater hardware configurations.

This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344 and by the LLNL LDRD program under Project Number 24-ERD-048.

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.

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2:45pm **AP+PS+TF-TuA-3 Atomic Layer Etching in HBr/He/Ar/O$_2$ Plasmas***,* ***Qinzhen 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$_2$. 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$_{DC}$ substrate self-bias. The coupled effects of O$_2$ addition and substrate self-bias DC voltage on etching rate were also explored. Etching slowed or stopped with increasing O$_2$ addition. As bias power was increased, more O$_2$ could be added before etching stopped.

3:00pm **AP+PS+TF-TuA-4 Comparisons of Atomic Layer Etching of Silicon in Cl$_2$ 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$_2$ 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$_2$ as a dosing gas was used for etching Si (100) samples. Optical emission spectroscopy was used to follow relative yields of SiCl, SiCl$_2$, SiBr and SiBr$_2$, and scanning electron microscopy and profilometry were used to measure etching rates. HBr and Cl$_2$ 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$_2$, 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$_2$ were injected into the reactor with the plasma on, etching occurs for both sources, with Cl$_2$ having a higher etching rate. When HBr or Cl$_2$ were fed to the reactor with the plasma off, only Cl$_2$ 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$_2$ by Plasma Fluorination and Oxygenation***,* ***Sanne Deijkers****, C. Palmer, N. Chittock, E. Kessels, A. Mackus,* Eindhoven University of Technology, The Netherlands

Molybdenum disulfide (MoS$_2$) is a two-dimensional (2D) transition metal dichalcogenide (TMD) with applications in catalysis and nanoelectronics.$^{1-3}$ 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--$_2$.[4] In this work, we present a plasma ALE process to etch crystalline MoS$_2$. 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.[5] As plasmas are more reactive than their gaseous counterparts, they are expected to allow for etching crystalline materials.

Fluorination was performed by a SF$_6$-based plasma, and as removal step various oxygen sources were tested. To avoid continuous etching of the MoS$_2$, the plasma composition of the fluorination step had to be optimized.[6] Addition of H$_2$ to the plasma mixture reduces F radical concentration by creating HF species *in situ*.[7] With an adequate H$_2$ content using a ratio of SF-$_6$:(SF$_6$+H$_2$) < 0.3, continuous etching is suppressed, and only modification of the top surface takes place. As second half-cycle, H$_2$O, O$_2$ gas and O$_2$ plasma exposures were tested. Of these only an O$_2$ plasma resulted in etching, while dosing H$_2$O or O$_2$ gas resulted in no measurable thickness change. Raman measurements showed a strong decrease in the characteristic E$^1_{2g}$ and A$_{1g}$ peaks, indicating etching of crystalline MoS-$_2$. The complete ALE recipe with saturated SF-$_6$-based plasma and O$_2$ plasma exposures had an EPC of 1.1 ± 0.2 Å at 300 °C table temperature.

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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$_2$/Ar$^+$ 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 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_2 using Sequential Exposures of $Al(CH_3)_3$ and H_2/SF_6 Plasma***, **David Catherall**, A. Hossain, A. Minnich,* California Institute of Technology

On-chip photonic devices based on SiO_2 are of interest for applications such as microresonator gyroscopes and microwave sources. Although SiO_2 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_2 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_2 using sequential exposures of $Al(CH_3)_3$ (trimethylaluminum, TMA) and $Ar/H_2/SF_6$ 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_2 and higher rates for ALD, PECVD, and sputtered SiO_2 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_2 plasma treatment. This process could find applications in smoothing of SiO_2 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_2 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 O2 or O3 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 O2/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 H2 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 O2 plasma. In both cases, in the infrared spectra, we observed absorption bands related to CF3 (1240 cm^{-1}), C=C, and C=O (1645 cm^{-1}) 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(hfac)2 and H2O. The subsequent O2 plasma half-cycle simply removes the hfac 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(hfac)2 and H2O. 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_2-plasma-based processes, allowing a subtractive metal patterning to be used. Current Ru etching processes largely rely on O_2/Cl_2-based RIE. While this process is able to anisotropically etch Ru, it requires Cl_2 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_2 plasma exposure can be reduced in H_2 plasma. Bias applied to the substrate during the H_2 step results in the selective reduction of RuN on the vertically-exposed surface, leaving a layer of RuN on the sidewalls. During the O_2 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_2 plasma etch to become anisotropic, while maintaining a high selectivity vs. SiO_2 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_2 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_2 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_2 plasma, more than 15 times less than the etch rate of Ru in O_2 plasma at the same conditions. Removal of the N_2 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_2 plasma. H_2 plasma was also found to significantly affect the etching of hard mask SiO_2. Reduction of the plasma density by lowering the power and increasing the pressure was necessary to reduce SiO_2 etching and corner faceting during the H_2 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_4 than the ALE process.

5:15pm **AP+PS+TF-TuA-13 Leveraging Plasma Nitridation for Atomic Layer Etching of Ni_3Al***, **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 absorber layer materials like Ni_3Al to mitigate mask 3D effects. However, Ni_3Al adoption has been limited by difficulties in anisotropically etching

Ni$_3$Al with high selectivity to the underlying Ru capping layer. A previously reported ALE based on plasma oxidation was shown effective at etching Ni$_3$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[1], and in this work the nitridation-based ALE process is extended to the more complex and industrially relevant Ni$_3$Al. X-ray photoelectron spectroscopy (XPS) is used to analyze the surface composition of blanket Ni$_3$Al films after plasma nitridation, showing the nitrided films have a stoichiometry of Ni$_{2.4}$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$_3$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$_3$Al etch compared to the vertical Ni3Al etch using scanning electron microscopy (SEM).

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5:30pm **AP+PS+TF-TuA-14 Precision Etching for Vertical GaN Nanowire Transistor Fabrication: A Focus on Atomic Layer Etching***, **Amin Karimi**, R. Jafari Jam, I. Sharma, O. Danielsson, M. Asif, Y. Ilarionova,* AlixLabs A.B., Sweden*; A. Kumar, P. Ramvall,* RISE Research Institutes of Sweden*; D. Suyatin, J. Sundqvist,* AlixLabs A.B., Sweden

Power electronics are essential for our daily lives, driving everything from consumer gadgets to industrial machinery. Gallium Nitride (GaN) stands out in this domain for its superior electrical properties, offering higher efficiency and power density compared to traditional silicon-based devices. Vertical GaN nanowire (NW) high-electron-mobility transistors (HEMTs) represent the forefront of GaN-based technologies, boosting advantages such as increased power density, reduced switching losses, improved heat dissipation, enhanced breakdown voltage, scalability, and radiation hardness. Despite these benefits, conventional fabrication techniques for GaN NW transistors face challenges. Non-uniform mask etching can lead to variations in NW diameters, impacting device performance. Reactive ion etching (RIE), which is often used for mask etching, may damage the substrate surface, compromising interface quality and device functionality. Surface irregularities exacerbate electron scattering, increasing energy dissipation and degrading electrical interfaces. Addressing these issues, atomic layer etching (ALE) emerges as a solution. ALE operates at the atomic level, removing one layer at a time without harming the substrate. Unlike traditional methods, ALE ensures a high-quality interface for improved device performance.

In our study, we utilize ALE to enhance the fabrication of GaN NW-based HEMT transistors. Our method employs fluorine-based chemistry for uniform SiN mask etching, enabling precise pattern transfer, and facilitating uniform NW growth. Additionally, we introduce chlorine-based ALE to refine substrate surfaces, reducing roughness and improving device performance. AFM characterization reveals a substantial decrease in surface roughness, directly contributing to enhanced electrical performance. We use Retarding Field Energy Analyzer (RFEA) data to optimize ALE parameters for different etching steps, and enhancing device fabrication.

In conclusion, our study highlights the potential for ALE processes to improve GaN NW-based HEMT transistor fabrication. By addressing mask uniformity and substrate surface roughness issues, ALE enables the production of GaN devices with superior interface quality and enhanced electrical performance.

Aknowledgemtn The ALL2GaN Project (Grant Agreement No 101111890) is supported by the Chips Joint Undertaking and its members including the top-up funding by Austria, Belgium, Czech Republic, Denmark, Germany, Greece, Netherlands, Norway, Slovakia, Spain, Sweden and Switzerland.

Electronic Materials and Photonics
Room 114 - Session EM+2D+BI+QS+TF-TuA

Advances in Photonic Materials and Devices

Moderators: Leland Nordin, University of Central Florida, **Philip Lee**, University of Kentucky

2:15pm **EM+2D+BI+QS+TF-TuA-1 New Materials for Metamaterials: Electrochemical Materials and Switchable Chiral Nanostructures***, **Vivian Ferry**,* University of Minnesota **INVITED**

Alternative materials for metasurfaces enable new properties and lay the foundation for advantage applications. This talk will discuss two strategies for new, tunable metasurfaces. The first part of the talk will discuss the use of electrolyte gating to control the optical properties of materials, focusing on La$_{1-x}$Sr$_x$CoO$_{3-d}$ (LSCO) as an exemplary case. We fabricate electric double layer transistors using LSCO and an ion gel, and under application of positive gate voltage gating facilitates the formation and migration of oxygen vacancies, and a transition from a perovskite phase to an oxygen-vacancy-ordered brownmillerite phase. This is accompanied by substantial change in optical properties, as measured with spectroscopic ellipsometry. The talk will discuss how LSCO can be incorporated with metasurfaces to produce tunable optical response. The second part of the talk will discuss chiral metamaterials, and particularly novel materials comprised of nanopatterned, light emitting nanocrystals with simultaneous control over both directionality and polarization state.

2:45pm **EM+2D+BI+QS+TF-TuA-3 Optoelectronic Nanowire Neuron***, **Thomas Kjellberg Jensen**,* Lund University, Sweden*; J. E. Sestoft,* Niels Bohr Institute, Denmark*; D. Alcer, N. Löfström, V. Flodgren, A. Das,* Lund University, Sweden*; R. D. Schlosser, T. Kanne Nordqvist,* Niels Bohr Institute, Denmark*; M. Borgström,* Lund University, Sweden*; J. Nygård,* Niels Bohr Institute, Denmark*; A. Mikkelsen,* Lund University, Sweden

Three different semiconductor nanowires are combined into a single optoelectronic artificial neuron. In general, artificial neurons sum and weight input signals, and output a signal according to a non-linear function which may be sigmoid-shaped (a generalized artificial neuron is shown in Fig. 1a). Figure 1b schematically shows the artificial neuron realized using nanowires. Here, neural excitation/inhibition is achieved by balancing inputted light across two pin-diode nanowires outputting a summed voltage measured by a nanowire-based field-effect transistor (FET).

The false-colored electron microscope image shown in Figure 1c depicts the fabricated nanowire neuron. In Figure 1d we show the current measured across the FET nanowire as a function of laser beam position, demonstrating the excitatory and inhibitory behavior. Selectively illuminating the excitatory nanowire diode, the change in conductance follows a sigmoidal curve as a function of linearly increasing light intensity (Figure 1e) – the necessary non-linear part of a neural network. Taken together, these properties provide the device with the basic functionalities needed for a neuromorphic computing node [1,2]. Future measurements will explore the time-domain effects.

Our artificial neuron provides a promising future platform for combining diverse materials with low power consumption and significantly reduced circuit footprint, this way addressing critical limitations for future-proofing photonics-based applications in neuromorphic computing.

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3:00pm **EM+2D+BI+QS+TF-TuA-4 Modulation of Optical and Plasmonic Properties of Epitaxial and Precision Titanium Nitride Thin Films***, I. Chris-Okoro,* North Carolina A&T State University*; S. Cherono,* North Carolina A & T State Uni*; C. Martin,* Ramapo College of New Jersey*; V. Craciun,* National Institute for Laser, Plasma, and Radiation Physics, Romania*; S. Kim, J. Mahl, J. Yano,* Lawrence Berkeley National Laboratory*; E. Crumlin,* Lawrence Berkeley Lab*; **Dhananjay Kumar**,* North Carolina A & T State Uni

The present study arises from the need for developing negative-permittivity materials beyond commonly employed plasmonic metals (e.g., Au, Ag), which are often incompatible (i.e., low melting point, mechanically soft, chemically unstable) with real operating environments. This work reports a pulsed laser-assisted synthesis, detailed structural characterization using x-ray diffraction (XRD), x-ray photoelectron spectroscopy (XPS), x-ray absorption spectroscopy (XAS), Rutherford Backscattering spectroscopy (RBS), and plasmonic properties of three sets of TiN/TiON thin films. The first two sets of TiN films were grown at 600 and 700 °C under a high vacuum condition (≤2 ×10^{-7} Torr). The third set of TiN film was grown in the presence of 5 mTorr of molecular oxygen at 700 °C. The purpose of making these three sets of TiN/TiON films was to understand the role of film crystallinity and the role of the oxygen content of TiN films on their optical and plasmonic properties. The results have shown that TiN films deposited in a high vacuum are metallic, have large reflectance, and high optical conductivity. The TiN films, grown in 5 mTorr, were found to be partially oxidized with room temperature resistivity nearly three times larger than those of the TiN films grown under high vacuum conditions.

The optical conductivity of these films was analyzed using a Kramers-Kronig transformation of reflectance and a Lorentz-Drude model; the optical conductivity determined by two different methods agrees very well. The good agreement between the two methods is indicative of a reliable estimate of the absolute value of reflectance in the first place. The existence of significant spectral weight below the interband absorptions is shared between two Lorentzians, one around 250 cm^{-1} and one around 2,500 cm^{-1}. We discuss here the dependence of the two bands on the deposition conditions and their effect on the plasmonic performances of TiN/TiON thin films, in particular on the surface plasmon polariton (SPP) and localized surface plasmon resonance (LSPR) quality factors.

This work was supported by the NSF PREM on the Collaborative Research and Education in Energy Materials (CREEM) via grant # DMR-2122067 and the DOE EFRC on the Center for Electrochemical Dynamics And Reactions on Surfaces (CEDARS) via grant # DE-SC0023415.

3:15pm **EM+2D+BI+QS+TF-TuA-5 Nano-Focusing and Characterization of the OAM Beam Through an Optical Fiber Using Plasmonic Nanostructure**, ***Rohil Kayastha***, *W. Zhang, B. Birmingham,* Baylor University*; Z. Gao,* Texas A&M University*; J. Hu,* Baylor University*; R. Quintero-Torres,* UNAM, Mexico*; A. V. Sokolov,* Texas A&M University*; Z. Zhang,* Baylor University

Optical vortex beam has been used in many applications such as nanoscale imaging, telecommunication, sensing, and so on due to its unique azimuthal phase distribution. Many of these applications utilize optical fibers as a sensor or to propagate the beam to transmit data and information. The vortex beam carrying an orbital angular momentum (OAM) has a phase singularity giving the beam a doughnut intensity profile. Due to its helical wavefront nature, the vortex beam carrying OAM has also been used to distinguish the enantiomers of the chiral molecule. However, coupling efficiency remains a problem due to the size mismatch of the beam and the molecule. Our work uses vortex fibers with plasmonic nanostructures to nano-focus the vortex beam to enhance the coupling between light and chiral matter. To achieve this goal, characterization of vortex beam in free space and through vortex fiber (a polarization-maintaining ring core optical fiber), and fabrication of nanostructure on fiber facet were performed.

Generation and propagation of OAM beams were characterized in free space and through a vortex fiber. The free-space OAM beam was coupled and transmitted successfully through the vortex fiber with a pure and stable output beam. The helicity characterization and polarization analysis of the free-space and fiber-coupled output vortex beams showed consistent polarization and OAM. The direction of the phase front was maintained after propagation of the OAM through the vortex fiber, as observed from the spiral interference pattern. Nano-focusing of the OAM beam using nanostructure on the fiber facet was observed from the simulation. The circular array of plasmonic nanobars was fabricated on the fiber facet core, and the far-field image of the output OAM beam was observed after transmission through the fiber with the nanostructure. The near-field image of the nano-focused OAM beam on the fiber will be investigated using a near-field scanning optical microscope (NSOM). The focusing of the OAM beam on a fiber facet with the nanostructure could enhance the coupling efficiency of the beam with chiral molecules. The nano-focused OAM on the fiber could be used as a scanning and sensing probe for single-molecule chirality detection.

4:00pm **EM+2D+BI+QS+TF-TuA-8 Templated Block Copolymer Network Thin Films as 3D Chiral Optical Metamaterials: Connecting Finite-Difference Time-Domain and Self-Consistent Field Theory Simulations**, ***Emily McGuinness***, *B. Magruder, P. Chen, K. Dorfman, C. Ellison, V. Ferry,* University of Minnesota

Optical metamaterials, whose properties depend not only on material selection but also the spatial arrangement of the material, provide access to interactions with light that are not present in bulk materials alone. Block copolymer self-assembly is a scalable method for creating 3D spatially periodic nanoscale structures to act as metamaterial templates. The gyroid morphology, whose curved, percolating structure is composed of triply connected struts, possesses chiral elements such as helices in bulk and chiral structures at certain surface terminations. As a result of their chirality, when templated with a plasmonic material, gyroids exhibit circular dichroism (CD) with applications in anti-counterfeit as well as molecular and protein sensing. While many optical simulations of gyroids assume a perfect cubic structure, most applications utilize thin films whose processing results in distortions such as compression normal to the substrate or surface rearrangements due to interactions with interfaces. Distorted gyroids, as well as the growing library of additional network structures possible from block copolymer self-assembly, are increasingly challenging to model from a purely mathematical basis and require better basis in physical reality. Combining the output of polymer self-consistent field theory (SCFT) with finite-difference time-domain (FDTD) optical simulations enables the exploration of thermodynamically equilibrated structures for both distorted gyroids and expanded network geometries. This presentation will investigate the CD response of compressed double gyroid thin films as well as that of newly hypothesized network structures such as H^{181}. In the first example, compression of (110) oriented silver double gyroid thin films yields a switching phenomenon from left to right circularly polarized light preferential absorption, offering the potential for dynamic systems (**Figure 1a**). Mechanistically, this behavior depends both on the surface and sub-surface structures of the compressed double gyroids. In the second example, (001) oriented silver templated thin films of the newly computationally uncovered H^{181} structure are shown to support a broadband visible light CD response (spanning 200 nm) with a g-factor (CD normalized to average absorption) of at least 0.14 across that entire wavelength range (**Figure 1b**). Overall, this work moves the optical simulations of metamaterials from block copolymers closer those physically realized, introducing additional opportunities for engineering their optical response.

4:15pm **EM+2D+BI+QS+TF-TuA-9 Solution Processing of Optical Phase Change Materials**, ***Brian Mills***, Massachusetts Institute of Technology*; R. Sharma, D. Wiedeman,* University of Central Florida*; C. Schwarz,* Ursinus College*; N. Li,* Massachusetts Institute of Technology*; E. Bissell,* University of Central Florida*; C. Constantin Popescu,* massachusetts Institute of Technology*; D. Callahan,* Charles Stark Draper Laboratory, Inc.*; P. Banerjee, K. Richardson,* University of Central Florida*; J. Hu,* Massachusetts Institute of Technology

Chalcogenide optical phase change materials (O-PCM) serve as the functional material in a variety of non-volatile photonic devices, from reconfigurable metasurface lenses to tunable integrated photonic resonators. Although a handful of high figure of merit O-PCMs have been identified and implemented in prototype devices, the space of O-PCM composition remains relatively unexplored, precluding the possibility of application specific choices in material composition that optimize device performance. This is due, in large part, to the lack of time and cost efficient methods for O-PCM thin film deposition and characterization, for which vacuum chamber deposition is the most common method. In this work, we present the first implementation of a solution processing approach for O-PCM film synthesis and deposition, providing evidence of the method's viability in creating high quality, functioning O-PCM films with close adherence to target stoichiometry. This method serves as a robust platform for materials exploration of O-PCM composition and allows for the identification of candidate O-PCM, as well as an understanding of the effect of compositional changes in O-PCM optical and cycling properties.

4:30pm **EM+2D+BI+QS+TF-TuA-10 Effects of Ce Concentration on the Microstructural, Optical, and Luminescence Properties in Ce:GAGG Ceramic Phosphors**, ***William Bowman***, *S. Lass,* University of Central Florida*; F. Moretti, W. Wolszczak,* Lawrence Berkeley National Laboratory*; R. Gaume,* University of Central Florida

Efficient luminescence and optical quality are necessary phosphor attributes for applications such as down-conversion layers in photovoltaics and computed tomography. Cerium-doped gadolinium aluminum gallium garnet (Ce:GAGG) is highly applicable for these purposes. It has been shown in other garnet hosts such as Ce:YAG and Ce:LuAG that Ce concentration alters both the luminescence and optical properties of the materials. In the case of Ce:GAGG single crystals and Ce concentrations lower than 1 at%, radioluminescence decay constants decrease by increasing the Ce concentration while light yield reaches a maximum at 0.3 at%. For Ce:GAGG ceramics, the effect of Ce concentration on these properties has not been systematically investigated. There is at current no work on determining the solid solubility limit of Ce in GAGG, which is critical in controlling the development of secondary phases and subsequent optical quality.

This study aims to investigate the effects of Ce concentration on the microstructural, optical, and luminescence properties of GAGG optical ceramics with dopant concentrations in the 0.1at% to 10at% range. Transmission of the material increases with increasing Ce concentration up to 5.0at%. At the same time, the optical and luminescence properties of these samples show a complex evolution upon Ce concentration, highlighting the complex interplay among optical characteristics of the samples, concentration-related luminescence quenching phenomena, and charge carrier trapping defects.

This material is based upon work supported by the U.S. Department of Homeland Security under Grant Award Number 20CWDARI00038-01-00. The views and conclusions contained in this document are those of the authors and should not be interpreted as necessarily representing the official policies, either expressed or implied, of the U.S. Department of Homeland Security.

4:45pm **EM+2D+BI+QS+TF-TuA-11 Solution Based Processing of $Ge_2Sb_2Se_4Te_1$ Phase Change Material for Optical Applications**, ***Daniel Wiedeman**, R. Sharma, E. Bissel, P. Banerjee,* University of Central Florida*; B. Mills, J. Hu,* Massachusetts Institute of Technology*; M. Sykes, J. Stackawitz, J. Lucinec, C. Schwarz,* Ursinus College*; K. Richardson,* University of Central Florida

Chalcogenide based phase change materials are important for creating novel optical and photonic devices, improving on current devices for future applications. Solution processing, via dip coating, spin coating, or drop-casting, is a low-cost, high-throughput alternative method of depositing thin films, which allows for greater composition diversity. In this work, we performed a detailed systematic study of the solution derived drop-casted film of Ge2Sb2Se4Te1 alloy in an ethylenediamine and ethanedithiol mixture. The composition, morphology and structural properties of the films were analyzed by employing scanning electron microscopy, energy dispersive X-ray spectroscopy, Raman spectroscopy, and X-ray diffraction. Our findings provide insight into a potential route for scalable $Ge_2Sb_2Se_4Te_1$ films.

5:00pm **EM+2D+BI+QS+TF-TuA-12 Multi-Dimensional p-WSe_2/n-Ga_2O_3 Enhancement-Mode Phototransistors for Stand-Alone Deep-Ultraviolet Sensing**, *J. Kim, **Soobeen Lee**,* Seoul National University, South Korea

β-Ga_2O_3 is an ultra-wide bandgap (UWBG) semiconductor with a bandgap of 4.9 eV, resulting in a high breakdown field of approximately 8 MV/cm and a high Baliga's figure-of-merit. β-Ga_2O_3 is a promising material for deep-ultraviolet (DUV) photodetector (PD) applications due to its direct bandgap of 4.9 eV, excellent thermal stability, and high absorption coefficient. Self-powered β-Ga_2O_3 PDs can be realized through p-n heterojunction (HJ) field-effect transistor architectures, exhibiting normally-off operation owing to the depletion region in the β-Ga_2O_3 channel. With intrinsic n-type conductivity caused by unintentional doping and challenges in p-type doping, fabricating self-powered β-Ga_2O_3 PDs necessitates combining β-Ga_2O_3 with p-type semiconductors such as transition-metal dichalcogenides (TMDs), nickel oxide, or silicon carbide. Tungsten diselenide (WSe_2), one of the TMDs, stands out as a promising material with a high monolayer mobility of approximately 180 $cm^2V^{-1}s^{-1}$. Their dangling-bond-free surfaces provide an advantage in forming sharp interfaces with other materials in HJs. Moreover, efficient p-type doping of WSe_2 is achieved via charge transfer by utilizing the high electron affinity of its self-limiting oxide, sub-stoichiometric tungsten oxide (WO_{3-x}), which is used as a dopant.

In this work, we introduce normally-off p-WSe_2/n-β-Ga_2O_3 phototransistors and demonstrate their self-powered operation under 254 nm light. p-Type WSe_2 was realized through charge transfer doping of WO_{3-x} formed by O_3 treatment, and the p-type doping effect of this oxide was confirmed through electrical characteristics. The cross-sectional structure of the fabricated p-WSe_2/n-β-Ga_2O_3 phototransistors was analyzed, and the electrical and optical properties were evaluated before and after WSe_2 oxidation. The device demonstrated a responsivity of 2 A/W under 254 nm light without an external bias, surpassing the performance of previously reported p-n HJ-based β-Ga_2O_3 PDs. Furthermore, we investigate the enhanced optoelectronic performance of multi-dimensional β-Ga_2O_3 phototransistors with plasmonic metal nanoparticles. In this presentation, we will discuss the potential of the self-powered multi-dimensional DUV β-Ga_2O_3 PDs with improved performance and their prospects in practical applications.

This work was supported by Korea Institute for Advancement of Technology (KIAT) grant funded by the Korea Government (P0012451, The Competency Development Program for Industry Specialist) and the Korea Research Institute for defense Technology planning and advancement (KRIT) grant funded by Defense Acquisition Program Administration (DAPA) (KRIT-CT-21-034, and KRIT-CT-22-046).

Thin Films
Room 115 - Session TF1-TuA

Thin Films for Energy Applications II: Batteries

Moderators: Adriana Creatore, Eindhoven University of Technology, Netherlands, **Mark Losego**, Georgia Institute of Technology

2:15pm **TF1-TuA-1 Unlocking High Volumetric Energy Densities in LCO Cathode Materials through Atomic Layer Deposition**, ***Jaime DuMont**, M. Martinez, M. Herbert-Walters, A. Dameron, B. Hughes,* Forge Nano

For the last 40+ years lithium cobalt oxide (LCO) batteries have reigned supreme in consumer electronics. This chemistry is attractive for its ability to provide top tier energy density in applications that require faster, lighter, and longer lasting cells. With the expectation of at least a doubling of the global market demand for consumer electronics over the next 10 years, LCO performance will need to rise to meet the demands of an ever-changing marketplace. Enhancements will rely heavily on the ability of materials scientists to tease out more and more of LCO's available capacity without sacrificing stability and lifetime.

In this work, we will highlight how protective coatings grown using the thin film deposition technique atomic layer deposition (ALD) can unlock high volumetric energy densities in LCO cathode materials not yet realized by other commercially available technologies. Electrochemical testing and differential capacity analysis of cathode half cells at progressively wider voltage windows illustrate that ALD protects and stabilizes LCO against detrimental side reactions that cause capacity fade and increase internal resistance. Post-cycling SEM-EDX characterization from full cells show that Co dissolution can be significantly reduced when an ALD coating is deposited on the cathode and that this effect becomes more pronounced at elevated cut off voltages. EIS analysis results demonstrate that ALD protects LCO surfaces from detrimental phase transitions above a 4.5V upper cut off voltage, suppressing the formation of a spinel layer and shielding the surface from harmful reactions with the electrolyte. Together, these enhancements lead to cycling performances that rival the best performing commercial material investigated in this work, showing that ALD can be a viable and affordable technology to meet the materials enhancement needs for the LCO cathode market.

2:30pm **TF1-TuA-2 Surface Chemistry of Plasma Exposure on Sulfide Solid Electrolytes**, ***Alexander Kozen**,* University of Vermont*; Y. Wang, D. Fontecha, G. Rubloff, S. Lee,* University of Maryland, College Park

Sulfide solid state electrolytes (SSEs) are considered one of the most promising materials to replace liquid electrolytes in next-generation batteries due SSEs astonishing ionic conductivities. However, the high reactivity of sulfide SSE materials precludes direct contact with Li metal anodes. One approach to stabilize the sulfide SSEs is passivating the sulfide interface with thin films of stable chemical species, forming an artificial solid electrolyte interphase (ASEI) layer. Ideal passivation materials for the anode/SSE interface are generally comprised of Li_3N or LiF species, which are stable at Li metal potentials. Here, we investigate the impact of plasma treatment on sulfide SSEs, as well as deposition of plasma-based ASEI materials using atomic layer deposition (ALD).

I will discuss the implications of Ar, N_2, and NH_3 plasma exposures on sulfide solid electrolytes (LGPS, LPSCl) and the resulting surface chemical changes as determined by in-vacuo x-ray photoelectron spectroscopy (XPS) measurements. N_2 and NH_3 plasma exposure can cleave Li_2S surface bonds and replace them with Li_3N surface species, however due to a lack of Li available at the surface this coverage is limited to ~30% and cannot form complete ASEI layers. Additionally, I will report the changes in electrochemical behavior of these pellets in Li/SSE/Li symmetric cells. Due to the incomplete surface coverage of Li_3N species, the surface nitride passivation is reduced and still allows deleterious reactions to occur after contact with Li metal. These results indicate that for complete Li_3N surface coverage, additional Li species must be available on the sulfide SSE surface before plasma treatment. I will also discuss the initial stages of ALD ASEI layer deposition on the sulfide SSE materials and evaluate their protection efficacy.

2:45pm **TF1-TuA-3 Tuning the Composition and Structure of High Mobility Nasicon-Type Thin Films Through Atomic Layer Deposition*, Daniela R. Fontecha,*** University of Maryland College Park*; A. Kozen,* University of Vermont*; D. Stewart, G. Rubloff, K. Gregorczyk,* University of Maryland College Park

Fast Li^+ ion conducting thin film solid state electrolytes (SSEs) by atomic layer deposition (ALD) enable high power density, fast time constants, and high operating frequency regimes in solid state ionic devices. However, the ionic conductivity of thin film SSEs fabricated by ALD has been limited by material development challenges, phase purity concerns when dealing with tertiary and quaternary systems, and challenges related to crystallinity. These complexities require careful consideration of the material system, precursor selection, process parameters, and post-annealing conditions to realize ideal ALD thin-film SSE materials with ionic conductivities $>10^{-6}$ S/cm. Bulk oxide SSEs, such as $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$ (LATP) have a NASICON-type crystal structure, show high ionic conductivity when crystalline (10^{-3} S/cm), demonstrate air & water stability, and a high voltage stability window. ALD synthesis of LATP can be broken down into well-known constituent processes (e.g., Li_3PO_4, Al_2O_3, TiP_2O_7) which can be combined with respect to stoichiometric ratios.

LATP can be considered Al-doped $LiTi_2(PO_4)_3$ (LTP), in which Al^{+3} ions partially replace Ti^{+4} ions in the NASICON-type structure. This facilitates fast Li^+ ion conduction through the 3D network. With that in mind, an ALD process for LTP was first developed by alternating between Li_2O and TiP_2O_7 sub-processes. The Li_2O sub-process uses lithium *tert*-butoxide (LiO^tBu) as the lithium source and water to complete the surface reaction. The TiP_2O_7 sub-process uses titanium (IV) isopropoxide (TTIP) as the titanium source, trimethyl phosphate (TMP) as the phosphorous source, and water. The growth rate of LTP was measured to be 0.4 Å/cycle at 300 °C. By adjusting the ratio between Li_2O and TiP_2O_7 cycles, the Li concentration in LTP can be tuned between 8.4-34.3 at % Li.

A NASICON-type crystalline structure is achieved by post-annealing the LTP films between 650 °C – 850 °C. The ideal annealing temperature was found to be a function of Li-ion concentration. The resulting measured ionic conductivity of partially crystalline LTP thin films is $3.6x10^{-5}$ S/cm at 80 °C. In this talk, we will discuss the complex issues related to process parameters, stochiometric tunability, and the resulting ionic conductivity when exploring ternary and quaternary LTP/LATP metal phosphates phase space.

3:00pm **TF1-TuA-4 Unlocking Novel Chemistry in Atomic Layer Deposition: Transformative Insights from Trimethylaluminum Interactions with Battery Materials*, Donghyeon Kang,*** *A. Mane, J. Elam,* Argonne National Laboratory

Trimethylaluminum (TMA) stands as a keystone in atomic layer deposition (ALD), widely esteemed for its role in crafting aluminum-based coatings across diverse applications. Notably, TMA is used to produce Al_2O_3 with H_2O, AlF_3 with HF-pyridine, and Al_2S_3 with H_2S, adhering to well-defined ALD mechanisms. These processes have permeated various substrates, leading to ultra-thin Al-based coating layers, particularly within the realm of energy storage materials such as battery cathodes, anodes, and solid electrolytes.

Our research group has embarked on a profound exploration of TMA's ALD chemistry, unveiling captivating interactions with reactive metal substrates, solid-state electrolytes, and battery cathode materials. Interestingly, when subjected to Li-metal anodes, TMA deviates from conventional ALD pathways, engendering a carbon composite layer atop the Li metal. This unconventional behavior arises from the inherent reactivity of both TMA and Li metal, diverging from established ALD paradigms. Moreover, our investigations reveal TMA's propensity to engage with Li-based impurities on solid electrolyte and cathode surfaces, yielding protective layers with beneficial attributes. Astonishingly, despite TMA's extensive utilization, this phenomenon has eluded prior scrutiny.

In this presentation, we unveil our findings on the intricate chemistry between TMA and battery materials (Li-metal, cathode, solid electrolytes) elucidated through in-situ quartz crystal microbalance (QCM), high-resolution X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), and Raman spectroscopy studies. Furthermore, we demonstrate the transformative potential of these discoveries in the realm of battery materials surface treatment, offering tantalizing prospects for streamlined industrial applications.

3:15pm **TF1-TuA-5 Mapping Lithium Diffusion in Thin-Film V_2O_5 using Raman Spectroscopy*, Daniel MacAyeal,*** University of Vermont*; L. Tapia-Aracayo, S. Caverly, D. Stewart, G. Rubloff,* University of Maryland*; A. Kozen,* University of Vermont

Understanding lateral diffusion of lithium in thin-film solid-state battery (SSB) materials is critical to improving SSB performance, stability, lifespan, and architecture. Using model test structures of sputtered V_2O_5/W/LiPON, we use Raman spectroscopy peak shifts to map Lithium concentration in V_2O_5. We evaluate the diffusion of lithium from LiPON layers into thin-film V_2O_5, measure the impact of different sputter deposition process conditions on lateral lithium diffusion, and investigate the effects of post-annealing the fabricated test structures. We will discuss the benefits of front versus back-side Raman spectroscopy for analyzing masked devices and correlate Raman spectroscopy mapping to XPS data to confirm compositional accuracy. Additionally, we will discuss the impact of electrochemical cycling at C/10 on lateral Lithium diffusion for symmetric V_2O_5/LiPON/V_2O_5 devices. Lastly, we will discuss the important implications of the lateral spacing limitations of clustered SSB devices due to lateral diffusion and propose architectural design rules based on this diffusion behavior for optimized device performance.

Thin Films
Room 115 - Session TF2-TuA

Vapor Synthesis of Hybrid, Organic, and Polymeric Materials (VSHOP I)

Moderators: Mark Losego, Georgia Institute of Technology, **Adriana Creatore**, Eindhoven University of Technology, Netherlands

4:00pm **TF2-TuA-8 Roll-to-Roll Photoinitiated Chemical Vapor Deposition of Polymer Films for Liquid-Repellent Textiles*, Trisha Andrew,*** University of Massachusetts - Amherst*; W. Viola, E. Chalouhi,* Soliyarn **INVITED**

Textile manufacturers currently use fluorocarbon based coatings/finishes to produce the liquid repellency that is now expected of fabrics in many contexts, including sporting apparel, upholstery, wall/floor covering, and personal protective equipment. However, it is increasingly apparent that these fluorocarbon chemicals spread throughout the global environment and bioaccumulate in groundwater and aquatic ecosystems because they cannot be chemically degraded by either naturally occurring microorganisms or prevalent atmospheric/oceanic/aquatic reactions. Selected vacuum-based coating processes, such as sputter coating and plasma-enhanced chemical vapor deposition, have been periodically explored over the past three decades to produce fluorine-free liquid repellent textile finishes. To date, the capital equipment and maintenance costs of continuous-process sputter coaters and similar plasma-based coaters, which require ultrahigh vacuum levels ($<10^{-6}$ Torr) to function, is too prohibitive for the textile industry to feasibly adopt. Further, historic experience has revealed that ultrahigh vacuum dependent processes have limited applicability in high-throughput textile finishing due to the microfibers and lint generated by most commodity textiles as they travel through a continuous process coater, which contaminate the process chamber and prevent pump down.

Recently, research spun-out from the University of Massachusetts Amherst and matured by Soliyarn Inc. has validated the concept and manufacturing readiness of photoinitiated chemical vapor deposition (piCVD) as a sustainable process for textile finishing. piCVD is a low-vacuum process during which a photoinitiated chain growth polymerization reaction is enacted within a custom-designed reactor to produce surface-grafted, functional polymer coatings on a diverse selection of substrates, including synthetic and naturally-derived woven or knit fabrics. Informed monomer choice has lead to the development of fluorine-free polymer coatings that match or outcompete commercial water-repellent finishes. With informed selection of high quantum yield molecular photoinitiators and coupled mechanical engineering design to optimize vapor delivery to the fabric surface(s), piCVD can be executed over large areas in a continuous, roll-to-roll format under mild vacuum (<1 torr). During this talk, we will survey the major design features of our roll-to-roll piCVD coater, detail the learning milestones that lead to the conception, improvement and optimization of this system and highlight the properties of the liquid-repellent finishes created via piCVD.

4:30pm **TF2-TuA-10 Battery Separators with Ultrathin iCVD-Polymer Coatings Mitigate Polysulfide Crossover in Lithium-Sulfur Batteries***, **Ramsay Nuwayhid**, H. Ford, J. Yeom, C. Love, J. Long, R. Carter,* U.S. Naval Research Laboratory

Lithium-ion batteries are approaching theoretical energy limits, necessitating development of advanced battery chemistries for critical applications. Lithium-sulfur (Li-S) batteries are an attractive alternative, due to the high abundance of sulfur in the earth's crust and high capacity of sulfur cathodes based on the conversion reaction of sulfur (S_8) to Li_2S. A major challenge in the practical implementation of Li-S batteries is the dissolution of intermediate lithium polysulfides formed during the conversion reaction, which react with the Li anode and sulfur cathode to form impeding interphases leading to loss of active material and poor cycle life. To overcome this technical challenge, we employ initiated chemical vapor deposition (iCVD) to conformally coat porous polyethylene separators used in Li-S cells to shield polysulfide crossover from the sulfur cathode to Li anode and enhance cycling performance. A novel copolymer, poly(divinylbenzene-co-(dimethylaminomethyl)styrene) (pDVB-co-DMAMS), is synthesized by iCVD and optimized to maintain cross-linking ability through DVB while the DMAMS functions to mitigate adverse polysulfide dissolution via specific adsorption at amine moieties. We first evaluate the electrochemical properties of pDVB-co-DMAMS in Li/Li symmetric cells through electrochemical impedance spectroscopy (EIS), demonstrating that iCVD-coated separators significantly reduce cell resistivity compared to cells with bare separators. Conformal coatings from 40-400 nm are evaluated in Li-S cells, in which thicker coatings show superior shielding of polysulfide cross-over through electrochemical self-discharge tests and UV-VIS spectroscopy. Furthermore, XPS and SEM analysis of the Li metal anode post-cycling reveals less crossover of polysulfide species and a smoother surface morphology for cells with iCVD-coated separators. Ultimately, 40 nm coatings are demonstrated to be the optimal thickness, maintaining high porosity of the separator and enabling high capacity retention at high gravimetric rates based on sulfur loading. Overall, this work demonstrates iCVD as a promising technique to stabilize reactive interfaces in beyond Li-ion battery systems.

4:45pm **TF2-TuA-11 Synthesis and Characterization of Ion Beam Nano-Engineered Metal-Polymer Nanocomposite Thin Films for SERS Application***, **Jai Prakash**,* National Institute of Technology Hamirpur, India*; H. Swart,* University of the Free State, South Africa

Ion beam induced nano-engineering of thin film surfaces provides a unique way to tailor the surface properties for various functional applications. Ion beam induced sputtering and bi-layer interface mixing lead to nanopatterning of the surfaces with unique morphologies that are useful for a variety of applications. The present work deals with nanopatterning of thin noble metal films (deposited by e-beam evaporation) on polymer surfaces, deposited with different techniques, such as chemical vapour deposition or spin coating. Ion beam induced nano-engineering creates noble metal nanoparticles on surfaces or embedded nanoparticles within the polymer films. Such noble metal nanoparticles exhibit unique optical properties due to their localized surface plasmon resonance properties. Synthesis and characterizations (RBS, SIMS etc.) of such ion beam nano-engineered surfaces with unique optical properties for SERS applications will be discussed, with an emphasis on the role of ion beam synthesis and tailoring of surfaces.

5:00pm **TF2-TuA-12 In situ Analysis of Temperature Dependence During Molecular Layer Deposition of Polyurea***, **Wallis Scholl**,* Colorado School of Mines*; T. Lill, H. Singh, M. Wang,* Lam Research Corporation*; S. Agarwal,* Colorado School of Mines

The use of molecular layer deposition (MLD) in practical applications is hindered by the lack of a well-defined temperature window and low growth per cycle (GPC), which is often much less than one repeat unit of the polymer chain. Multiple studies report a lower GPC at higher deposition temperatures, and as a result MLD is typically conducted at room temperature.The mechanism behind this temperature dependence is not well understood; different sources attribute lower GPC at higher temperatures either to an increased rate of double reactions, where both functional groups in a bifunctional molecule react with the surface, or to a lower degree of physisorption of the growth precursors onto the film's surface. In this study, we used *in situ* attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy as well as *in situ* ellipsometry to monitor the film composition and thickness throughout MLD of polyurea film using toluene diisocyanate (TDIC) and ethylene diamine (ED) as precursors. The polyurea films were deposited at 0, 22, and 45 C. In agreement with previous literature (see Figure 1), over 25 MLD cycles, we observed a lower GPC at higher temperatures. The infrared spectra recorded during MLD reveal the temperature dependence of the chemical reactions and precursor physisorption. The amide I/II bands observed in the infrared spectra are related to the polyurea linkage, and indicate film growth. We find that the integrated absorbance for the amide I/II bands decreased with increasing temperature during both half cycles (see Figure 2). Further, we show evidence that precursor physisorption is the main cause for the temperature dependence of MLD. The two MLD precursors have different probability of double reaction and physisorption, and we typically observe a larger increase in integrated absorbance for the amide I/II modes during the TDIC half-cycles compared to the ED half-cycles. This discrepancy suggests that ED is more likely to physisorb than TDIC into the film and not form the polyurea linkages by reaction with the isocyanate groups. Additionally, the degree of physisorption of ED increases as the temperature is lowered. During the TDIC half-cycle, polyurea linkages are created due to chemical reaction between the physisorbed ED molecules. This also implies that to maintain a linear growth rate, as the temperature is lowered, site balance is achieved by a higher degree of double-reactions of TDIC.

5:15pm **TF2-TuA-13 Multi-Stimuli Responsive Sensors for Electronic Skin Applications***, **Anna Maria Coclite**,* University of Bari, Italy **INVITED**

Embedding sensors in smart architectures that record the response from the environment and transform it in a measurable signal is the objective of artificial skins. In this talk, a smart skin based on a single novel multi-stimuli responsive material, combining force, temperature and humidity sensing will be presented. The new sensor concept is realized by combining a hydrogel and piezoelectric zinc oxide (ZnO) in an array of core-shell structures.[1] This architecture is achieved thanks to the use of vapor-based technologies for material processing, i.e. initiated chemical vapor deposition, atomic layer deposition and nanoimprint lithography. We demonstrate that the skin can detect the stimuli with lateral resolution below the one of human skin. While the piezoelectricity of ZnO provides sensitivity to external force, the thermoresponsiveness of the hydrogel core provides sensitivity to surrounding temperature and humidity changes. The hydrogel core exerts mechanical stress onto the ZnO shell, which is translated to a measurable piezoelectric signal. A localized force sensitivity of 364 pC N^{-1} is achieved with very low cross talk between 0.25 mm^2 pixels. Additionally, the sensor's sensitivity to humidity is demonstrated at 25 and 40 °C, i.e., above and below the hydrogel's lower critical solution temperature (LCST) of 34 °C. The largest response to temperature is obtained at high humidity and below the hydrogel's LCST.

We also demonstrate that the use of a multi-chamber reactor enables performing the ZnO and hydrogel depositions, sequentially, without breaking the vacuum.[2] The sequential deposition of uniform as well as conformal thin films responsive to force, temperature and humidity improved the deposition time and quality significantly. Proper interlayer adhesion could be achieved via in situ interface activation, a procedure easily realizable in this unique multi-chamber reactor. Beyond the fabrication method, also the mechanical properties of the template used to embed the core-shell nanorods and the crosslinker density in the hydrogel were optimized following the results of finite element models. Finally, galvanostatic electrochemical impedance spectroscopy measurements showed how temperature and humidity stimuli have different effects on the device impedance and phase and these differences can be the base for stimuli-recognition.

Possible applications stem from robotics to smart prostheses. Smart skins could monitor human breathing, pulse and temperature or detect dehydration.

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 $In_xGa_{1-x}N$ 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 ℃, 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 $In_xGa_{1-x}N$ films on SiO_2/Si, quartz, and sapphire substrates using digital alloying technique in an HCP-ALD reactor at 200 ℃.

The $In_xGa_{1-x}N$ alloy films were deposited using conventional metal-alkyl precursors (triethylgallium, trimethylindium) and two different nitrogen plasmas (N_2/H_2, N_2/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. $In_xGa_{1-x}N$ 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 VO_2 (c-VO_2) undergoes a phase transformation between two crystalline states near room temperature (≈ 68 °C), which is accompanied by a metal-to-insulator transition (MIT). This favorable MIT in stoichiometric c-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 VO_2 films deposited by thermal atomic layer deposition (ALD) processes are amorphous and require a high temperature post-deposition annealing step (≥ 400 °C) to crystallize, which often limits the application space of ALD VO_2 due to thermal budget constraints. Thus, the development of processes to produce ALD c-VO_2 without the need of a high-temperature annealing step are desired.

Two possible routes to c-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 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 V_2O_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-VO_2, even under ambient conditions. Both methodologies maintain sub-200 °C temperature windows which facilitate the use of c-VO_2 in a wider range of applications. For example, high-temperature annealing of VO_2 on metal substrates often results in the dewetting of 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-VO_2. A focal point of the PEALD studies is correlating plasma properties, including plasma power, Ar/O_2 ratio, system pressure, and total gas flow during the plasma step, with the control of the 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 V^{4+}/V^{5+} ratio. fsLP is shown effective at producing c-VO_2 from amorphous ALD films under ambient conditions. We also discuss the ability of the technique to produce c-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***,* ***Yousra Traouli,*** *U. Kilic,* 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, $Zn(CH_3)_2$, 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°C ≤ T ≤ 300°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, SiO_2/Si, glass, sapphire, and quartz substrates. This process utilizes nickelocene ($NiCp_2$) and 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 (l=190-380 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.

9:00am **AP1+EM+PS+TF-WeM-5 Characterizing Inductively Coupled Plasmas in Ar/SF$_6$ 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$_6$) 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$_x^+$, SF$_y^-$, F$^-$, F$_2^+$, etc.) and reactive neutral species (SF$_x$, F, F$_2$, 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$_6$ 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$_3$) thin films grown via plasma-enhanced ALD using a remote ICP employing Ar/SF$_6$ 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.

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9:15am **AP1+EM+PS+TF-WeM-6 Dynamic Global Model of Cl$_2$/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$_2$/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$_2$ 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$_2$ plasma and the Ar activation plasma.

We closely investigate the influence of the switch duration between the Cl$_2$ 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$_2$ 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$_e$). These stiff T$_e$ 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.

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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$_4$) 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$_2$), ammonia (NH$_3$), or hydrogen (H$_2$) 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^2. 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$_4$ 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$_2$ produced the highest carbon etch rate at ~225 Å/min (Fig. 2). In contrast, NH$_3$ displayed a slower carbon etch rate of ~48 Å/min and H$_2$ 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$_2$ plasma which also oxidizes the surrounding and underlying material. Using H$_2$ 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$_2$O$_3$***, **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$_2$O$_3$ films were deposited at 300 °C using TMA and H$_2$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_2O 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.

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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

11:00am **AP2+EM+PS+TF-WeM-13 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 µDALP™ 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 µDALP™ 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 µDALP™ retains ALD's core advantages while enhancing scalability, processing speed, and cost-efficiency. We will highlight the transformative impact of µDALP™ 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, µDALP™, Nanotechnology, Thin Film, Microelectronics.

Fig. 1. (a)Top view of aligned Si trenches (aligned horizontally) coated with a perpendicular line of TiO2(low magnification SEM). (b) Microfluidic precursor delivery concept: Schematic view of the delivery nozzle in frontal view (top) and in cross-section (lower panel).

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11:15am **AP2+EM+PS+TF-WeM-14 Ceramic Thin-Film Composite Membranes with Tunable Subnanometer Pores for Molecular Sieving by Atomic Layer Deposition***, X. Zhou,* Yale University*; R. Shevate, A. Mane,* ***Jeffrey Elam,*** Argonne National Laboratory*; J. Kim, M. Elimelech,* Yale University

Membranes with tunable, sub-nanometer pores are needed for molecular separations in applications including water treatment, critical mineral extraction, and recycling.Ceramic membranes are a promising alternative to the polymeric membranes typically used in such applications due to their robust operation under harsh chemical conditions. However, current fabrication technologies fail to construct ceramic membranes suitable for selective molecular separations. In this presentation, we describe a ceramic thin film composite (TFC) membrane fabrication method that achieves sub-nm pore size control using atomic layer deposition (ALD) by incorporating a molecular-scale porogen.By co-dosing alkyl alcohols along with the H_2O coreactant during Al_2O_3 ALD, we incorporate alkoxide species in the film which create a continuous network of pores upon calcination.Varying the alkyl alcohol (methanol, ethanol, isopropanol) tunes the pore size.We use Fourier transform infrared absorption spectroscopy, X-ray photoelectron spectroscopy, and scanning electron microscopy to elucidate the surface chemistry and growth during the alcohol-modulated ALD as well as the subsequent pore formation.We evaluate the transport and separations properties of the ALD TFC membranes using a two-chamber diffusion cell with aqueous salt solutions.We measured a remarkable enhancement in the transport of Cl^- compared to SO_4^{2-} (8.6 times faster) matching the selectivity of state-of-the-art polymer membranes.We attribute this selectivity to the dehydration of the large divalent ions within the subnanometer pores. In addition, permeation studies using neutral adsorbates revealed average pore sizes of ~7Å, 13Å, and 19Å for ALD TFC membranes prepared using methanol, ethanol, and isopropanol, respectively.This work provides the scientific basis for the design of ceramic membranes with subnanometer pores for molecular sieving using ALD.

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_{3-x} NP films with photochemical stability enhanced by Ta_2O_5 ALD[1] and superhydrophilic and antireflective TiO_2/SiO_2 NP films with elastic modulus and hardness enhanced by Al_2O_3 ALD.[2] Applications of such nanocomposite films, however, are limited by their small thickness (typically a few µm 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_2 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_2 NP compacts with ZnO:Al is accomplished via a recently developed cyclical-temperature ALD process.[3] The ZnO:Al-coated SiO_2 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.[4] An EC-PAS process with a maximum pressure of ~2 GPa and a maximum temperature of 450 °C yields dense SiO_2/ZnO:Al nanocomposites that contain nanocrystalline ZnO:Al networks and exhibit low electrical resistivity, ρ. At nominal ZnO:Al coating thicknesses, t, of ~3 nm and ~6 nm, ρ is on the order of 1 and 0.1 Ω-cm, respectively, at 300 K. Moreover, at $t \approx$ 6 nm, the Hall mobility approaches 1 $cm^2V^{-1}s^{-1}$ at 300 K, and ρ 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.

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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_2O_3 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 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_3 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 (λ = 100-200 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_6/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_6/Ar plasma, produced with an inductively coupled plasma (ICP) source, were used as our precursor and reactant for the ALD AlF_3 process. Optimization of the ALD parameters was performed, and our best ALD AlF_3 films (F/Al ≈ 3, ~1% oxygen content, and roughness < 1 nm) were attained using 100 W ICP power and total plasma gas flows > 30 sccm. Our ALD AlF_3 films provide improved FUV reflectivity compared to oxidized bare Al, however, these optical properties are still limited by Al oxide at the AlF_3/Al interface. To overcome this, we utilize our in-situ e-beam plasma, produced in a gas mixture of SF_6/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_6/Ar ratio and flow, sample bias) and how they affect the AlF_3 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 (≈90% at 121 nm). We then discuss hybrid AlF_3 films, in which the growth is initiated by e-beam plasma, and then continued using an optimized ALD AlF_3 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_3 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.

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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 $Al_xSc_{1-x}N$ exhibits strong potential for utilization in NVM devices operating at very high temperatures (> 500 °C) given its stable and high remnant polarization (P_R) above 100μC/cm^2 with demonstrated ferroelectric transition temperature (T_C) > 1000 °C. Here, we demonstrate an $Al_{0.68}Sc_{0.32}N$ 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+}) (+/- 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 μC/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 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 °C will also be presented in the meeting.

[a] 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_2, 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 ^{18}O tracers to evaluate the diffusion coefficient of oxygen in the ferroelectric phase. Hafnium zirconium oxide films containing ^{16}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 ^{18}O-containing hafnium zirconium oxide film was deposited via thermal atomic layer deposition with ^{18}O provided from a $H_2{}^{18}O$ source. Tracer anneals were then performed and the ^{18}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} cm^2/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.

8:30am **EM+AIML+AP+QS+TF-WeM-3 Thin Film Physics of Ferroelectric HfO_2 and ZrO_2 - From Laboratory Demonstrations to Semiconductor Chips***,* *P. Lomenzo, **Uwe Schroeder,*** Namlab, Germany **INVITED**

Integrated ferroelectric devices for non-volatile memory applications have been undergoing pioneering developments in recent years due to the CMOS-compatible and highly scalable ferroelectricity exhibited by HfO_2- and ZrO_2-based thin films. A unique hallmark of these industry-friendly ferroelectric materials is the underlying fluorite crystal structure that contains a rich polymorphic landscape in which polar and antipolar crystal phases can be stabilized with unique ferroelectric, pyroelectric, and piezoelectric properties. Obtaining high performance ferroelectric properties for electronic device applications in HfO_2 and ZrO_2 thin films is contingent upon the single-phase formation of the ferroelectric *Pca*2_1 orthorhombic phase, which is challenging due to the competing formations of the nonpolar monoclinic and tetragonal phases. Chemical doping, film thickness, film stress, film growth processing parameters, annealing conditions, defects, and the encapsulating device (i.e., electrodes, interfaces) can all influence the structure and functional electrical behavior of these ferroelectrics.

Due to the extremely scaled film thickness (< 4 nm) and the unique fluorite structure these ferroelectric materials exhibit, tremendous developments in material and device physics have taken place over the past decade. Not only are the underlying intrinsic ferroelectric properties critical for ferroelectric HfO_2- and ZrO_2-based devices, but the interaction between the ferroelectric thin film and the electrodes is much more prominent than conventional, thicker perovskite ferroelectrics. While the coercive field and remanent polarization are nominally determined by the intrinsic film properties of ferroelectric fluorites, extrinsic factors, such as oxygen vacancies and interfacial layers, frequently influence these important ferroelectric parameters that dramatically affect the read/write energy and memory window of ferroelectric random access memory (FeRAM) technologies, respectively. Moreover, reliability challenges such as read/write endurance and retention in both FeRAM and ferroelectric field effect transistors (FeFETs) non-volatile memory technologies involve the intricate coupling between the ferroelectric film, electronically active defects, operation scheme, and the device structure itself.

An in-depth overview is given of current state-of-the-art developments in both the material and device physics of ferroelectric HfO_2 and ZrO_2 thin films. Physical insights obtained from laboratory-scale experiments and devices are compared and contrasted with chip-level demonstrators of non-volatile memories incorporating these novel fluorite ferroelectric thin films.

9:00am **EM+AIML+AP+QS+TF-WeM-5 Iridium Etching: ExploringReactive Ion Etching Parameters for Efficient Electrode Fabrication inFerroelectric Memory***,* ***Yanan Li,*** *P. Bezard, 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+AIML+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 (HfO_2) and alloyed hafnia zirconia thin films $(Hf,Zr)O_2$ 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 °C, coercive fields close to 1 MV/cm, and ferroelectricity down to ~ 1nm, 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 $Hf_{0.5}Zr_{0.5}O_2$ 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 °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 µm to 117 µm. Fig. 2 (a) shows these J-V sweeps for a 100 µm 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 µm 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+AIML+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) incongruency 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 remenant 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 MV cm^{-1} field also showed dependence of $P\text{-}_r$ 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 a non-volatile memory devices.

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

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 vonNeumannarchitectureshave poor area and computationalpowerefficiency and longexecutionlatency.CIMarchitectureswithMultiplyAccumulateMacros(MAMs)canaddressthe power and performancelimitationsof approaches that use von Neumann hardware architectures. To date these MAM implementationshavebeenhinderedbythelargephysicalsizeofmemoryelementsandthehigh-powerconsumptionofsupportingcircuitry.The Defense Advanced Research Program Agency’s OptimumProcessingTechnologyInsideMemoryArrays(OPTIMA)programseekstodeveloparea-andpower-efficienthigh-performanceMAMswithinnovativesignalprocessingcircuits. 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_2 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[1], but analog in-memory computing hardware can reduce the energy required by up to six orders of magitude[2]. 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 $TiO\text{-}_2$ are discussed with and without a capping Nafion film. It is observed that the anatase TiO_2 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^+ insertion kinetics. Subsequently, TiO_2 is used in an all-solid-state three electrode transistor by splitting the bottom current collector into a source-drain configuration and using PdH_x as the counter electrode and H^+ reservoir. Results toward novel solid state anatase TiO_2 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_2) 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_2-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_2-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 peed, and non-destructive readout. Recent progress in FeFETs based on two-dimensional (2D) semiconductor channels and ferroelectric $Al_{0.68}Sc_{0.32}N$ (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 um^{-1}, along with stable memory retention over 10^4 s and endurance greater than 10^4 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.

Magnetic Interfaces and Nanostructures
Room 121 - Session MI+2D+AC+TF-WeM

Altermagnetism and Spin-Dependent Systems

Moderators: Markus Donath, Muenster University, Germany, **Valeria Lauter**, Oak Ridge National Laboratory

8:00am **MI+2D+AC+TF-WeM-1 Twisted Electrons in Momentum Space: A Photoemission Perspective on Spin and Orbital Angular Momentum in Quantum Materials*, Maximilian Ünzelmann,*** University of Würzburg, Germany*; B. Geldiyev,* Univsersity of Würzburg, Germany*; T. Figgemeier,* University of Würzburg, Germany*; H. Bentmann,* NTNU Trondheim, Norway*; F. Reinert,* Univsersity of Würzburg, Germany **INVITED**

Beyond the spin, electronic states in crystalline solids can exhibit finite expectation values of orbital angular momentum (OAM). This phenomenon has attracted considerable attention in recent years and can particularly be traced back to the following key applications: (i) Since OAM is formed solely by inversion symmetry breaking (ISB) – and thus can also be present without magnetism or strong spin-orbit coupling (SOC) – it appears as an interesting quantum degree of freedom raising the potential of orbital analogs to spintronic phenomena, i.e. the field of *orbitronics*. (ii) OAM has been proposed to be a useful observable to assess nontrivial topology in the band structure of topological quantum matter. Lastly, if the atomic SOC strength is sizable, OAM is coupled to the electron spin giving rise to rich spin and orbital momentum space textures.

In this talk, I will shed light on those textures from the perspective of angle-resolved photoemission spectroscopy (ARPES). Combining ARPES with light-polarization-dependent and spin-resolved measurements allows us to address the momentum-dependent properties of the spatial and spin part of the wave functions, respectively. I will present experimental results on model-like monolayer systems and topological quantum materials and show that – as well as how – the complex interplay of ISB and SOC forms striking spin-orbital textures. Based on these findings, I will discuss the potential of utilizing OAM (i) towards orbitronic transport and (ii) to detect unexpected topological features.

8:30am **MI+2D+AC+TF-WeM-3 Falicov Student Award Finalist Talk: Gap Tuning by Hole Doping in EuZn2As2 Semimetal*, Dejia Kong*[1]*,*** University of Virginia*; S. Karbasizadeh,* University of South Carolina*; G. Narasimha,* Oak Ridge National Laboratory*; P. Regmi,* University of South Carolina*; C. Tao,* Oak Ridge National Laboratory*; S. Mu,* University of South Carolina*; R. Vasudevan,* Oak Ridge National Laboratory*; I. Harrison,* University of Virginia*; R. Jin,* University of South Carolina*; Z. Gai,* Oak Ridge National Laboratory

$EuZn_2As_2$ is an ideal candidate for topological magnetism study in comparison to other europium-based semimetals that exhibit a similar type of magnetic transition from the antiferromagnetic phase to the ferromagnetic phase at a low temperature. [1] Theoretical calculations predict gapped and flatter bands in $EuZn_2As_2$ but a gapless Γ point in $EuCd_2As_2$. [2] In this work, a low-temperature cleaved $EuZn_2As_2$ crystal is studied using scanning tunneling microscopy/spectroscopy (STM/S) and density functional theory (DFT). A group of triangular-shaped defects in combining with the DFT calculations are used to identify the existence of the europium-terminated and arsenic-terminated surfaces at the cleavage. Large bandgaps are observed on the two pristine terminations. However, the bandgap width is found to be very sensitive to local heterogenous, like defects and step edges. Two defect groups that create local electron deficiency, i.e. substitutional defect of As replacing Zn, and Zn vacancy, can drastically lower the bandgap. Furthermore, the modification of the bandgap width shows a discrepancy on the two terminations, bigger on Eu termination but much smaller on As-Zn termination. So, we predict that purposely hole doping the system during the crystal growth stage may create a new topological semimetal material with a gapless europium layer sandwiched by a gapped As-Zn lattice.

Reference:

1 Blawat, J. *et al.* Unusual Electrical and Magnetic Properties in Layered EuZn2As2. *Adv Quantum Technol* **5** (2022).

2 Wang, Z. C. *et al.* Anisotropy of the magnetic and transport properties of EuZn2As2. *Phys Rev B* **105** (2022).

8:45am **MI+2D+AC+TF-WeM-4 Characterization of $LaMnO_3$/$SrTiO_3$ Thin Films and Its Mn Valance State Correlated with Ferromagnetism*, Ghadendra Bhandari,*** *P. Tavazohi, V. Dewasurendra, M. Johnson, M. Holcomb,* West Virginia University

Thin films of $LaMnO_3$ (LMO) / $SrTiO_3$ (STO) perovskite have gained interest for their abilities to be an essential component of some heterostructures while still exhibiting an interesting magnetic phase diagram. We have grown $LaMnO_3$ thin films on $SrTiO_3$ using pulsed laser deposition and deposition has been monitored by reflection high energy electron diffraction (RHEED) to verify layer-by-layer growth. Structure and magnetic properties have been characterized by X-ray diffractometry (XRD), and vibration sample magnetometry (VSM). LaMnO3 thin films exhibit ferromagnetic FM phases whereas bulk LaMnO3 is antiferromagnetic A-type. All thin films are coherently strained, forcing them to have the in-plane lattice parameter of the STO substrate (3.905 Å), but the out-of-plane parameter varies (3.89-3.93 Å). The variation in the c-lattice is developed from O_2 growth pressure and consequently the Mn cation is in mixed valence state $Mn^{3+/4+}$. The valence state of the Mn cation is realized from XPS and XAS study. The ferromagnetic magnetization is originated by the double exchange of Mn^{3+}-O-Mn^{4+}. The thickness averaged magnetizations from PNR measurements are comparable with magnetization obtained from VSM. The strength of magnetization correlates with content of Mn^{4+}.

9:00am **MI+2D+AC+TF-WeM-5 Altermagnetism: From Spintronics to Unconventional Magnetic Phases*, Libor Šmejkal,*** Uni Mainz, Germany **INVITED**

The search for unconventional quantum phases that break the symmetries of the crystal lattice has been a focus in physics since the early days of quantum theory, driven by both fundamental interest and potential applications. Prominent examples include cuprate superconductors, which are known for their unconventional d-wave Cooper pairing, and dissipationless transport.

In this presentation, we will discuss our recent discovery[1] of an unconventional magnetic phase motivated by our earlier predictions and observations of unconventional spintronics effects [2,3,4]. This unconventional phase, altermagnetism (see Figure), unlike common ferromagnetism and antiferromagnetism,breaks the symmetries of the crystal lattice, and features d, g, or i-partial wave characteristics simultaneously in its spin and electronic structure[1]. D-wave altermagnetism thus represents magnetic analogue of d-wave superconductivity.

We identified altermagnetism by employing and developing a symmetry framework that considers paired transformations involving electron spin and the crystal lattice. This framework is emerging as a new paradigm in the study of magnetic crystals. We will demonstrate its usefulness by discussing (i) the altermagnetic band structure of the semiconductor MnTe, which we recently experimentally observed through collaborative work using photoemission spectroscopy[5], and (ii) our identification of more than 240 realistic altermagnetic candidates.

Additionally, we will explore the rapid expansion of altermagnetic concepts to many fields with focus on ultrafast spintronics memories[6], dissipationless transport [2-4] and two-dimensional band topology [7]. Finally, we will outline the latest developments in the field, including the theoretical identification of the magnetic analog of superfluid helium-3 and we will propose transport experiments which can be used for its detection[8].

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[2] L. Šmejkal, et al., Sci. Adv. 6, eaaz8809 (2020)

[3] I. Mazin ,et al., PNAS 118, e2108924118 (2021)

[4] H. Reichlová,et al., Nature Communications 15, 4961 (2024)

[5] J. Krempasky*, L. Šmejkal*, S. Souza*, et al., Nature, 626, 517 (2024)

[6] L. Šmejkal et al., Phys. Rev. X 12, 011028 (2022)

[7] I. Mazin, R. Gonzalez-Hernandez, and L. Šmejkal, arXiv:2309.02355 (2023)

[8] Birk Hellenes, et al., arXiv:2309.01607v2 (2024)

9:30am **MI+2D+AC+TF-WeM-7 Growth Study of Kagome-structured Mn_3Sn on Gallium Nitride (000_1) Using Molecular Beam Epitaxy***, H. Hall, S. Upadhyay, T. Erickson, A. Shrestha, A. Abbas,* ***Arthur Smith,*** Ohio University

Over the past few years, there has been a large amount of interest in Kagome-structured magnetic materials with non-collinear antiferromagnetic ordering [1]. Such materials show interesting magnetic

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[1] **Falicov Student Award Finalist**

properties including anomalous Hall effect and topological Hall effect [2]. In recent work, we have reported growth of Mn_3Sn on sapphire (0001) which resulted in either *a*-plane or *c*-plane film orientations [3,4]. The substrate however was not ideal, and frequently we observed the disappearance of the diffraction pattern upon opening the Mn and Sn shutters with the pattern reappearing after some amount of resting time. In the case of the *c*-plane orientation, theory suggested this could be due to interfacial disordering of the lattice. This might be due to the ~19% lattice mismatch which also is one reason for the preferred growth of *a*-plane oriented Mn_3Sn on sapphire (0001) due to the much smaller lattice mismatch (<5%) along that direction. Nonetheless, high quality films prove difficult to obtain on sapphire (0001), and a better substrate is desirable. As such, we have investigated the growth of Mn_3Sn films on freshly grown gallium nitride surfaces. The Mn_3Sn growth follows immediately after the growth of N-polar GaN (000$\underline{1}$), thus giving a perfectly clean and well-ordered substrate surface with only ~2.66% lattice mismatch along the 30° line to the high symmetry axis of GaN. We have investigated this as a function of substrate temperature and find an optimal temperature range in which streaky and clear RHEED patterns are obtained from the beginning of the growth. Next plans include studying of this surface with high-resolution STM and spin-polarized STM. This research has been supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering under Award No. DE-FG02-06ER46317.

[1] H. Yang *et al.,* New J. of Physics **19**, 015008 (2017).

[2] S. Nakatsuji, N. Kiyohara, and T. Higo, Nature **527**, 212 (2015).

[3] S. Upadhyay *et al.*, J. Vac. Sci. & Technol. A **41**, 042710 (2023).

[4] S. Upadhyay *et al.,* Surfaces and Interfaces **42**, 103379 (2023).

9:45am **MI+2D+AC+TF-WeM-8 Exchange Bias Effect in Single-Layer Antiferromagnetic Mn3GaN Films***, **Ali Abbas**, A. Shrestha,* Ohio University*; D. Russell, F. Yang,* The Ohio State University*; A. Smith,* Ohio University

Strain-induced spin structures in non-collinear antiferromagnetic materials like Mn_3GaN can be controlled by an external magnetic field[1][2]. In this work, we report the intrinsic exchange bias in the "single" antiferromagnetic Mn_3GaN films fabricated by epitaxial growth of Mn_3GaN on MgO (001) substrate using molecular beam epitaxy under *in–plane* tensile and *out–of–plane* compressive strain. Scanning transmission electron microscopy confirms significant strain at the Mn_3GaN/MgO interface due to substrate induced tetragonal distortion. Superconducting quantum interference device measurements reveal an exchange bias field (Heb=1225 Oe) and a vertical magnetization shift below 300 K. Furthermore, magnetization M vs. the applied field H measurements from 300K down to 50K reveal the consistent horizontal and vertical shift of the hysteresis loop, which are usually observed only in ferro–/antiferromagnetic bilayers. Here, the exchange bias effect may be attributed to strain, leading to canted and uncompensated Mn spins coupled with an upper antiferromagnetic region, as reported in another system [2][3]. The findings of strain–induced exchange bias in antiferromagnetic Mn_3GaN films may open a new route/ novel system for spintronic properties by design. This research has been supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering under Award No. DE–FG02–06ER46317 (work done at Ohio University, not including XRD) and under award No. DE–SC0001304 (XRD and SQUID measurements done at The Ohio State University).

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[2] B. Cuiet al., "Strain engineering induced interfacial self-assembly and intrinsic exchange bias in a manganite perovskite film". Scientific reports, 3(1), 2542, (2013).

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11:00am **MI+2D+AC+TF-WeM-13 L-Gap Surface Resonance at Pt(111): Influence of Atomic Structure, d Bands, and Spin-Orbit Interaction***, **Markus Donath**, F. Schöttke, P. Krüger,* University of Münster, Germany*; L. Hammer, T. Kißlinger, M. Schneider,* University of Erlangen-Nürnberg, Germany

Pt(111) hosts a surface resonance with peculiar properties concerning energy vs momentum dispersion and spin texture. At variance with the free-electronlike behavior of the L-gap Shockley-type surface states on the fcc(111) surfaces of Au, Ag, and Cu, it splits into several branches with distinct spin polarization around the center of the surface Brillouin zone. Theoretical predictions based on density-functional theory vary depending on the particular functionals used. To clarify this issue, we investigate the atomic structure of Pt(111) by low-energy electron diffraction and the unoccupied electronic structure by spin- and angle-resolved inverse photoemission. The experimental results are backed by theoretical studies using different functionals which show that the characteristics of the surface band depend critically on the lattice constant. We identified a delicate interplay of several contributions: Lattice constant, hybridization with d bands, and the influence of spin-orbit interaction are critical ingredients for understanding the peculiar energy dispersion and spin character of the unoccupied surface resonance.

11:15am **MI+2D+AC+TF-WeM-14 Substrate-Induced Strain Effects on $SrFeO_3$ Thin Films***, **Lucas Barreto**,* University of Pennsylvania*; P. Rogge, J. Wang, B. Lefler,* Drexel University*; D. Puggioni, J. Rondinelli,* Northwestern University*; S. Koroluk, R. Green,* University of Saskatchewan, Canada*; S. May,* Drexel University

Materials with non-trivial magnetic ordering give rise to exotic topological phenomena that can enhance spin-based devices' performance. In this scenario, the cubic perovskite $SrFeO_3$ exhibits a rich magnetic ordering, described by a multi-**q** magnetic arrangement. In this work, we evaluate how in-plane lattice stress influences the structural, magnetic, and electronic of $SrFeO_3$ films. We grow epitaxial $SrFeO_3$ films on different substrates to induce compressive and tensile strains, characterize them using X-ray diffraction, and probe the electronic transport as a function of temperature. The experimental data are supported by density functional theory calculations, from which we obtain the structural and electronic properties of the strained $SrFeO_3$ structure. We map the magnetic ordering via resonant x-ray magnetic diffraction and observe shifts in the projection of the magnetic wavevector **q** along the [111] direction. Our results indicate that the lattice strain can tune the magnetic propagation vector on the films while maintaining the $SrFeO_3$ metallic behavior.

Thin Films
Room 115 - Session TF-WeM

Vapor Synthesis of Hybrid, Organic, and Polymeric Materials (VSHOP II)

Moderators: Trisha Andrew, University of Massachusetts - Amherst, **Siamak Nejati**, University of Nebraska-Lincoln

8:00am **TF-WeM-1 Chemical Vapor Deposition of Metalloporphyrins: Engineering and Integration of Advanced Conjugated Polymers for Catalysis and Sensing***, **Nicolas Boscher**,* Luxembourg Institute of Science and Technology (LIST), Luxembourg **INVITED**

Porphyrins have been intensively investigated as catalysts and sensing materials. The properties of porphyrin-based catalysts and sensors can be tailored from the careful selection of the central metal ion chelated at the centre of the macrocycleand its peripheral substituents. Beyond, several studies have highlighted the cooperative effect promoted by conjugated covalent links between porphyrins on both their catalytic and sensing properties. However, in spite of the many synthetic approaches developed towards the synthesis of porphyrin-based conjugated assemblies, the engineering and integration of porphyrin-based conjugated assemblies has been limited by their weak solubility.

Oxidative chemical vapor deposition (oCVD) was recently demonstrated as a convenient method for the simultaneous synthesis and deposition of porphyrin-based conjugated polymers.[1] Porphyrins possessing free *meso*-positions[1-4] and/or free *beta*-positions[5] and porphyrins bearing thienyl or aminophenyl substituents[6] have both been successfully polymerised using oCVD to yield the formation of formation fused porphyrin tapes and bridged porphyrins covalent organic frameworks, respectively. Importantly in the perspective of practical application, including heterogeneous electrocatalysis and gas sensing, the porphyrin-based conjugated polymers are readily deposited on virtualy any substrate in the form of smooth and thickness-controlled thin films.

Up-to-date, porphyrin-based conjugated polymer thin films prepared by oCVD have been successfully investigated for the electrochemical hydrogen evolution reaction,[2] nitrate reduction reaction,[6] oxygen reduction reaction,[6] oxygen evolution reactions.[3] In addition, porphyrin-based conjugated polymer thin films prepared by oCVD have also been successfully investigated as chemiresistive sensors for ammonia detection.[4] Experimental and theoretical data demonstrate the impact of both the central metal cations and substituents on the catalytic activitiesand sensing properties of the porphyrin conjugated polymer thin films.[2-6] The approach reported in this work circumvents many limitations of solution-based approaches and pave the way to the facile engineering and integration of efficient electrocatalysts and selective sensing materials from porphyrins.

[1] Bengasi *et al.*, *Angew. Chem., Int. Ed.* **2019**. [2] Huerta-Flores *et al.*, *ACS Appl. Energy Mater.* **2020**. [3] Bansal *et al.*, *J. Mater. Chem. A* **2023**. [4] Bengasi *et al.*, *Adv. Elect. Mat.* **2020**. [5] Bansal *et al.*, *Chem. Eur. J.* **2024**. [6] Mohamed *et al.*, *Adv. Mater.* **2024**.

8:30am **TF-WeM-3 Introducing Non-Covalent Interactions during initiated Chemical Vapor Deposition (iCVD)**, ***Rong Yang***, Cornell University

Initiated Chemical Vapor Deposition (iCVD) has been increasingly studied in the solvent-free synthesis and manufacturing of polymeric thin films. It eliminates bulk solvents, thus improving the environmental sustainability of polymer synthesis. Its scalability points to a new pathway for accelerating the development and environmentally friendly manufacturing of polymeric nanomaterials. While prior research has predominantly leveraged the all-dry and low-pressure reaction environment to achieve ideal gas behavior and thereby controlled synthesis conditions, recent advances in iCVD synthesis have unlocked an opportunity to depart from the ideal gas regime. In this talk, I will discuss our results on introducing non-covalent interactions to preorganize molecules and access new chemical synthesis pathways to broaden the palette of attainable polymer chemistry and morphologies. Leveraging hydrogen bonding, we demonstrated that complexing 4-vinylpyridine with hexafluoroisopropanol could increase the polymer molar mass by 700%, which in turn led to unprecedented material hardness and surface morphologies. Building from this demonstration, we tackled the challenge of undesirable chain transfer (e.g., to the imidazole group during the polymerization of 1-vinylimidazole), which has limited the synthesis of an important class of amine/imidazole-containing polymers using iCVD polymerization. Using 1-vinylimidazole as an example, we protonated the transfer-to location via a vapor complexation with acetic acid, rendering the chain transfer energetically unfavorable and enabling synthesis of poly(1-vinylimidazole) films with unprecedented purity, molar mass, and highly controllable polymerization kinetics. This new synthetic capability, in turn, led to the discovery of a novel bioactive material.

8:45am **TF-WeM-4 oCVD PEDOT Thin Film as the Hole Transport Layer in Perovskite Solar Cellto Enhance Device Stability and Performance**, ***Meysam Heydari Gharahcheshmeh***, San Diego State University/ Department of Mechanical Engineering

Stability concerns have hindered the practical use of perovskite solar cell (PSC) devices. One significant factor contributing to this issue is the inherent acidity of the commonly used hole transport layer, poly(3,4-ethylene dioxythiophene):polystyrene sulfonate (PEDOT:PSS), potentially jeopardizing the stability of PSC devices. To address this challenge, this study explores employing oxidative chemical vapor deposition (oCVD) with antimony pentachloride (SbCl5) as a liquid oxidant for fabricating PEDOT-Cl thin film. This technique is utilized to create stable and ultrathin PEDOT films with high conformity, presenting a promising alternative as a hole transport layer in PSCs. The resulting oCVD-grown PEDOT-Cl thin films, showcase exceptional optoelectronic properties, precise nanostructure control, stability, and integration capabilities. These attributes establish them as a robust and effective choice to be used as the hole transport layer in PSC device. Integration of oCVD PEDOT-Cl thin films as the hole transport layer in PSCs yields a remarkable power conversion efficiency (PCE) of 20.74%, surpassing the 16.53% PCE achieved by spin-coated PEDOT:PSS thin films treated with dimethyl sulfoxide (DMSO) as a polar solvent. Additionally, PSCs incorporating oCVD PEDOT-Cl thin films exhibit a noteworthy 2.5× improvement in stability compared to their PEDOT:PSS-DMSO counterparts.

Keywords: Oxidative Chemical Vapor Deposition, PEDOT, $SbCl_5$ Oxidant, Perovskite Solar Cells

9:00am **TF-WeM-5 Networking Density Effects on the Patterning Performance of Metal-Organic Resists Deposited via Hybrid Molecular Layer Deposition**, ***Long Viet Than***, *G. D'Acunto, S. Bent,* Stanford University

The implementation of extreme ultraviolet (EUV) lithography in semiconductor manufacturing promises to extend Moore's Law by enabling the patterning of sub-20 nm feature sizes. However, further device scaling is dependent on the implementation of EUV-tailored photoresists that meet requirements in sensitivity, resolution, and line edge roughness. With feature sizes approaching the nanometer scale, stochastic variation in the photoresist molecular structure also affects pattern quality, resulting in the need for new resist chemistries with uniform chemical distribution.

Metal-organic thin films deposited via hybrid molecular layer deposition (MLD) are a promising class of materials to address the challenges of designing new EUV-compatible resist chemistries, by incorporating EUV-absorbing metal centers into the polymer network while exhibiting Å-level thickness control and atomic-scale homogeneity. In this work, we investigated a series of hybrid MLD-derived aluminum alkoxide (alucone) resists, deposited via trimethylaluminum (TMA) and a series of alcohol counter-reactants (glycerol, ethylene glycol, and sequential dosing of methanol/ethylene glycol). This process yielded thin films that are chemically akin, as demonstrated by x-ray photoelectron spectroscopy (XPS), but exhibit notable differences in networking/crosslinking density. The resist performance was evaluated via electron beam lithography, a well-established proxy for EUV. The alucone resists exhibited negative-tone patterning, attributed to the loss of organic ligands and alumina formation resulting from electron-induced reactions. Decreasing the crosslinking density enhanced the resist contrast, thus improving the resolution. On the other hand, increasing the crosslinking density resulted in drastically reduced developer solubility. The variation observed between these hybrid materials underscores the importance of structure-property relationships for the rational design of metal-organic EUV resists.

9:15am **TF-WeM-6 Synthesis of Disulfide Polymer by Oxidative Molecular Layer Deposition (oMLD)**, ***Amit K. Datta***, University of Missouri, Columbia; *N. Paranamana, P. Kinlen, M. Young,* University of Missouri-Columbia

Poly-2,5-dimercapto-1,3,4-thiadiazole (pDMCT) is a redox-active polymer consisting of heterocyclic monomer units connected by disulfide bonds. pDMCT has been used as a battery material, biocide, and corrosion inhibitor. Upon electrochemical reduction, the disulfide bonds in pDMCT break to form thiolate anions that readily coordinate with cations, providing lithium ion conductivity for battery applications and allowing for capture of heavy metal cations. In this work, our goal is to study the vapor-phase formation of thin films of pDMCT using oxidative molecular layer deposition (oMLD) for use as a protective coating in solid state lithium-ion batteries. We employ alternating vapor exposures of the 2,5-dimercapto-1,3,4-thiadiazole (DMCT) monomer and a molybdenum pentachloride ($MoCl_5$) chemical oxidant to perform oMLD growth in a custom viscous-flow reactor at 150 °C and ~1 Torr. We employ *in situ* quartz crystal microbalance (QCM) studies during growth to understand the film growth chemistry, as well as *ex situ* spectroscopic and electrochemical characterization to confirm formation of pDMCT. QCM studies and *ex situ* thickness measurements indicate controlled linear growth. We examine the effect of precursor dose times on polymer chain length, and the effect of polymer chain length and film thickness on electrochemical properties. The controlled growth of ultrathin films of pDMCT shows promise for the application of this chemistry as a protective coating for lithium-ion battery applications and for passive uptake of heavy metal ions. More broadly, these studies establish that oMLD can be used to create polymers connected by disulfide linkages, opening a new class of polymers accessible by oMLD synthesis.

9:30am **TF-WeM-7 High-Throughput MLD for Advanced EUV Photoresists: Stability and Performance of Organic-Inorganic Hybrid Films**, ***Duncan Reece***, University of Washington, UK; *E. Crum, A. Dao, J. Keth, D. Bergsman,* University of Washington

The development of sub-5nm semiconductor architectures requires photoresists that efficiently absorb Extreme Ultraviolet (EUV) light, maintain structural integrity under high-energy exposure, and are sufficiently thin for precise patterning while being robust enough to withstand the processing environment. Molecular Layer Deposition (MLD) is exceptionally well-suited for this purpose due to its precise control over film composition and thickness, which is crucial for tailoring photoresist properties to meet the stringent specifications of next-generation lithography.Using our previously published high-throughput multi-chamber MLD system, we investigated the stability and mechanical properties of organic-inorganic hybrid thin films designed for EUV lithography applications. MLD's capability to layer angstrom-thick films precisely enables the creation of photoresists that are both thin enough for advanced lithographic detail and durable against developers and etchants.We synthesized 18 different film chemistries using combinations of three organometallic precursors—diethyl zinc, trimethylaluminum, and tin(IV) t-butoxide—and six organic precursors: ethylene glycol, 1,2,4-trihydroxybenzene, 1,5-hexadiene-3,4-diol, 2-butyne-1,4-diol, cis-2-butene-1,4-diol, and 2-methylenepropane-1,3-diol. These films were evaluated for stability in air, developer compatibility, and etchant resistance, both before and after UV exposure. Candidates exhibiting enhanced properties post-exposure were further assessed for mechanical robustness using Atomic Force Microscopy and nanoindentation.Further characterization involved Fourier Transform Infrared Spectroscopy and X-ray Photoelectron Spectroscopy to elucidate degradation pathways and confirm structural integrity. Understanding these pathways is essential for assessing film stability and performance. Selected materials demonstrating optimal performance profiles underwent patterning tests using an electron beam source, with results visualized via Scanning Electron Microscopy.Our findings reveal that specific combinations of organic and inorganic components yield films with significantly improved mechanical properties and stability in air and potential developers. This research primarily aims to understand why certain combinations result in superior film properties, providing valuable insights into the development of advanced EUV photoresists. By emphasizing the fundamental aspects of material behavior, we highlight the efficacy of high-throughput MLD in the rapid screening and optimization of photoresist materials, advancing semiconductor technology.

9:45am **TF-WeM-8 Development of a 300mm Wafer Scale Molecular Layer Deposition Process***, C. Vallee, **Van Long Nguyen,*** University at Albany-SUNY*; O. Sathoud, D. Newman, J. Sathoud, J. McAdams, C. Wajda, K. Tapily, G. Leusink,* TEL Technology Center America

Molecular layer deposition (MLD) is an advanced technique for depositing polymeric thin film at the molecular level control. In comparison to the well-known sister method for depositing inorganic thin film, the atomic layer deposition (ALD), research on MLD is still relatively limited in applications, especially in the semiconductor industry, due to the difficulty in finding suitable precursors. Organic precursors for MLD processes are typically low volatility, stability, and reactivity, which is a critical bottleneck limiting its utilization in high-volume semiconductor manufacturing that is based on 300mm wafer process platforms. In this paper, we report the development of a MLD process using a 300mm wafer process tool. MLD of polyamide, nylon 2,6, was first developed at 85ºC using two precursors which are ethylene diamine (ED) and adipoyl chloride (AC). While ED has high vapor pressure providing growth saturation easily, low volatility AC precursor requires longer dosing times to reach the growth saturation and is the critical one for optimizing the growth per cycle (GPC) of our MLD process on the 300mm wafer tool (**Figure 1a**). Furthermore, the bubbling dosing mode is more effective in delivering AC to the chamber in comparison to the vapor-draw dosing mode. Our optimized MLD process shows linear growth of 0.12 nm/cycle with 15 cycles of nucleation delays on the Si wafer (**Figure 1b**). The uniformity of the deposition until 120 cycles was less than 4.8% across a 300mm Si wafer. The process is undergoing further optimization to improve GPC, uniformity, and processing time. Ellipsometry, AFM, ATR-FTIR, and XPS are key techniques for the characterization of the film growth for our MLD process.

11:00am **TF-WeM-13 Area Selective Deposition of Ferrocene-Functionalized Thin Films***, J. Lomax,* The University of Western Ontario, Canada*; E. Goodwin,* Carleton University, Canada*; J. Bentley,* The University of Western Ontario, Canada*; M. Aloisio, C. Crudden,* Queen's University, Canada*; S. Barry,* Carleton University, Canada*; **Paul Ragogna,*** The University of Western Ontario, Canada **INVITED**

Ferrocene is a stable molecule with well understood redox activity, and has been utilized extensively in areas such as bio-sensing, organometallic chemistry, and materials science.$^{1–3}$ This work leverages the utility of ferrocene precursors for solution and vapour phase depositions that prepare ferrocene-based thin films. There was an affinity for the deposition to occur selectively on metallic substrates, and therefore the area-selective deposition of ferrocene-containing precursors was demonstrated, which has potential applications for onwards application in nanoscale device fabrication.^{4} Preparation of the small molecule precursors will be discussed as well as the analysis of the fabricated thin film/monolayers via X-ray photoelectron spectroscopy (XPS), Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS), Atomic Force Microscopy (AFM), surface Raman spectroscopy, and X-ray Reflectivity (XRR)

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11:30am **TF-WeM-15 Infiltration of Methanol Vapor Induces Lattice Flexibility in Microporous $Ni_2(BDC)_2$DABCO Thin Films***, **Greg Szulczewski,*** The University of Alabama

Thin films of $Ni_2(BDC)_2$DABCO, where BDC is benzendicarboxylic acid and DABCO is 1,4-diazabicyclo[2.2.2]octane, were made by a hot vapor-assisted conversion technique. The thin films were characterized by x-ray diffraction, vibrational spectroscopy and scanning electron microscopy. The polycrystalline films were determined to be phase pure by powder x-ray diffraction. Infrared and Raman spectroscopy reveals the carboxylic acid ligands were converted into carboxylates. The films were activated by heating under high vacuum and adsorption/desorption isotherms were measured for several volatile organic compounds, including alcohols, nitrobenzene, toluene, and methyl iodide vapors at room temperature. The isotherms revealed a Type I behavior for ethanol, isopropanol, toluene nitrobenzene, and methyl iodide vapors. In contrast, the isotherm for methanol has a characteristic S-shape, which is characteristic of a flexible lattice. The adsorption isotherm for methanol has distinct steps, which is attributed to lattice expansion. Upon removal of methanol from the thin film, the lattice relaxes back to the original structure. The results are compared to other pillared microporous coordination compounds.

11:45am **TF-WeM-16 Nanomolecularly-Induced Kinetic, Chemical, and Morphological Effects During Thin Film Synthesis of Hybrid Inorganic/Organic Nanolaminate Multilayers***, **Collin Rowe**, G. Sharma,* Materials Science and Engineering Department, Rensselaer Polytechnic Institute*; A. Devos,* Institute of Electronics, Microelectronics and Nanotechnology, CNRS UMR 8250, France*; H. Pedersen,* Department of Physics, Chemistry, and Biology, Linköping University, Sweden*; G. Ramanath,* Materials Science and Engineering Department, Rensselaer Polytechnic Institute

Molecular nanolayers (MNLs) at inorganic thin film interfaces are known to improve chemical stability, and stimulate completely unexpected mechanical responses and electrical and thermal transport behaviors[1]. Stacking inorganic/organic thin film interfaces with nanoscale proximity, e.g., in high-interface-fraction multilayers, offers promise to access emergent properties via superposition of nanomolecular effects. Synthesizing such structures requires low-temperature depositions of high-quality ultrathin inorganic nanolayers to preserve the integrity of the MNLs. Here, we will demonstrate the synthesis of titania/organo-diphosphonate[2] and AlO_xN_y/hydroquinone multilayers with sharp interfaces by sequential atomic- and molecular-layer deposition (ALD/MLD) cycles. Our results from electron microscopy, X-ray diffraction, and ion beam and photoelectron spectroscopy measurements show that MNLs can significantly alter the inorganic nanolayer growth rate, composition, surface roughness, and phase stability. Examples include up to ~50% decrease in titania growth rates by diphosphonate MNLs, and near complete aluminum nitride to oxide conversion by hydroquinone MNLs. Atomistic mechanisms underpinning these changes will be discussed in terms of the impact of the MNL backbone structure and terminal chemistry on the surface reaction pathways. Acoustic pump-probe spectroscopy measurements on our hybrid multilayers reveal unusual acoustic damping responses which will be described in terms of the MNL interface chemistry and nanolayer periodicity. Further understanding and harnessing such MNL-induced effects and their correlations with emergent properties is crucial for designing high-interface-fraction hybrid nanolaminates for applications.

[1] *Engineering inorganic interfaces using molecular nanolayers*, G. Ramanath, C. Rowe, G. Sharma, V. Venkataramani, J. G. Alauzun, R. Sundararaman, P. Keblinski, D. G. Sangiovanni, P. Eklund, H. Pedersen, **Appl. Phys. Lett.** 122, 260502 (2023).

[2] *Nanomolecularly-induced effects at titania/organo-diphosphonate interfaces for stable hybrid multilayers with emergent properties*, C. Rowe, A. Kashyap, G. Sharma, N. Goyal, J. G. Alauzun, S. T. Barry, N. Ravishankar, A. Soni, P. Eklund, H. Pedersen, G. Ramanath, **ACS Appl. Nano Mater.** (2024).

12:00pm **TF-WeM-17 The Impact of Copolymer Molecular Sequence on Electronic Transport***, **Mahya Mehregan,*** University of Missouri-Columbia*; J. Schultz, M. Maschman, M. Young,* University of Missouri, Columbia

Conjugated polymers (CPs) have garnered significant attention for application in electronics and electrochemical devices, including supercapacitors, solar cells, electrochromics, batteries, microelectronics, and sensors.Blending different conjugated monomers together into copolymersprovides a powerful platform for controlling CP properties.However, torationally improve the performance of conjugated copolymers in these electronic and electrochemical applications, a fundamental understanding of how copolymer structure influences electronic transport is necessary. Conventional synthesis methods for CPs provide poor control over the short-range molecular structure, or sequence, of copolymers, making it difficult to understand the role of short-range molecular structure on electronic transport.Here, we employ vapor-phase oxidative molecular layer deposition (oMLD) at 150°C and ~1 Torr to deposit thin films of conjugated copolymers one monomer at a time, providing control over the copolymer molecular sequence. Because oMLD is a vapor deposition technique, these polymers are also chemically pure with no side-chains or additives.In this study, we specifically control the molecular sequence of copolymers of 3,4-ethylenedioxythiophene (EDOT) and pyrrole (Py) by adjusting the dosing scheme of EDOT and Pymonomers during oMLD growth. Using this synthesis approach, we establishnew insights into how short-range molecular structureinfluences electronic transport through these copolymers. Specifically, we find:(1)a departure from the rule of mixtures, where the block length of each homopolymer within the copolymer influences the overall electronic conductivity even at a constant overall composition; and (2) evidence for a critical hopping distance (or quasi-Debye length) between conductive domains, where electronic conductivity decreases by multiple orders of magnitudewhen the spacing between conductive domains is greater than this critical distance. The fundamental insights into the electronic conductivity through conjugated copolymers we describewill inform the design of conjugated copolymers for electronic and electrochemical devices. More broadly, this study demonstrates thatoMLDcan be used as a platform for polymer materials discovery by synthesizing copolymers with precise control of molecular sequence.

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 specularity. To achieve this, our group has developed and characterized heteroepitaxial Ru(0001) thin-films deposited on Al_2O_3(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_2O) eliminates the rate limiting step of conventional MBE to the growth of In_2O_3—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^{2+}-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. Guguschev, 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_2), temperature T_s = 100-600 °C, and substrate [Al_2O_3(0001), MgO(001) and SiO_2/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_2 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 ρ vs thickness d = 5 – 1000 nm for single-crystal Co(001)/MgO(001) layers indicates an effective electron mean free path λ_{eff} = 27± 2 nm at 295 K and a room-temperature bulk resistivity ρ_o = 6.4 ± 0.3 μΩ-cm. At 77 K, the reduced electron-phonon scattering yields a smaller ρ_o = 1.3 ± 0.1 μΩ-cm and a larger λ_{eff} = 79 ± 6 nm. The resulting benchmark quantity $\rho_o\lambda_{eff}$ = 17.4×10^{16} and 10.2×10^{16} Ω-m^2 at 293 and 77 K, respectively, is 4-6 times larger than the first-principles predictions. The measured ρ_o 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 $\rho_o\lambda_{eff}$ 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 μm, 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 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 μA/μm for nMOS and 0.8 μA/μm 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_2O_3 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 x10^{13} cm^{-2} of vertical geometry NiO/β-Ga_2O_3 heterojunction rectifiers produced carrier removal rates in the range 120-150 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 ~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_2O_3 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_2O_3, 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_2 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 nanolaminate-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_x - 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_x while varying thickness of individual layers. Second, a set of films were made by dosing small amounts of TiO_x 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 AVS National Student Award Finalist Talk: Determination of Band Offsets at the Interfaces of NiO, SiO_2, Al_2O_3 and ITO with AlN***, **Hsiao-Hsuan Wan**[1], 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_2/AlN, Al_2O_3/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_2 /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_2O_3/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_2 is an attractive candidate for surface passivation or gate dielectric formation on AlN. Given the band alignment of the Al_2O_3, 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.

Magnetic Interfaces and Nanostructures
Room 121 - Session MI+2D+AC+TF-WeA

2D Magnetism and Magnetic Nanostructures

Moderators: Mikel Holcomb, West Virginia University, **Tiffany Kaspar**, Pacific Northwest National Laboratory

2:15pm **MI+2D+AC+TF-WeA-1 Interface Tunable Magnetism in Transition Metal Telluride Thin Films and Heterostructures***, **Hang Chi**,* University of Ottawa, Canada **INVITED**

Novel quasi-2D magnets are attracting much attention recently. In situ prepared sharp interfaces are desirable for strain engineering and/or hybridizing with other quantum systems, enabling fundamentally new phenomena and opportunities for spintronics [1]. Ferromagnetic Cr_2Te_3 ultrathin films, optimally grown on Al_2O_3(0001) and $SrTiO_3$(111) using molecular beam epitaxy, manifest an extraordinary sign reversal in the anomalous Hall conductivity as temperature and/or strain are modulated. The nontrivial Berry curvature in the electronic-structure momentum space is believed to be responsible for this behavior [2]. Furthermore, when proximitized with $(Bi,Sb)_2Te_3$-type topological insulator, via the Bloembergen-Rowland interaction, magnetic ordering in monolayer Cr_2Te_3 is favorably enhanced, displaying an increased Curie temperature [3]. Combining ab initio simulation, advanced scanning tunneling microscopy, magnetic force microscopy, transmission electron microscopy, magneto transport and particularly depth-sensitive polarized neutron reflectometry, Cr_2Te_3 has been established as a far-reaching platform for further investigating the marriage of magnetism and topology. These findings provide new perspectives to the magnetic topological materials in general, that are topical for the future development of topological spintronics.

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Acknowledgment

We acknowledge the support of the Natural Sciences and Engineering Research Council of Canada (NSERC) Discovery Grant RGPIN-2024-06497.

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[1] **AVS National Student Award Finalist**

2:45pm **MI+2D+AC+TF-WeA-3 AVS National Student Award Finalist Talk/Falicov Student Award Finalist Talk: Probing Intrinsic Magnetization Dynamics of the $Y_3Fe_5O_{12}$/Bi_2Te_3 Interface at Low Temperature***, A. Willcole,* Sandia National Laboratories, USA*; V. Lauter,* Oak Ridge National Laboratory, USA*; A. Grutter,* National Institute of Standards and Technology (NIST)*; C. Dubs,* INNOVENT e.V. Technologieentwicklung, Germany*; D. Lidsky,* Sandia National Laboratories, USA*;* ***Bin Luo***[1,2]*,* Northeastern University, US*; M. Lindner, T. Reimann,* INNOVENT e.V. Technologieentwicklung, Germany*; N. Bhattacharjee,* Northeastern University, US*; T. Lu, P. Sharma, N. Valdez, C. Pearce, T. Monson,* Sandia National Laboratories, USA*; M. Matzelle, A. Bansil, D. Heiman, N. Sun,* Northeastern University, US

Topological insulator-magnetic insulator (TI-MI) heterostructures are essential in spintronics, enabling magnetization control via topological surface state-induced spin orbit torque. However, many TI-MI interfaces often face issues like contamination in the magnetic insulator and a low-density transitional region in the topological insulator, which obscure the system's intrinsic properties. In this study, we addressed these challenges by depositing sputtered Bi_2Te_3(BT) on liquid phase epitaxy grown $Y_3Fe_5O_{12}$ (YIG)/$Gd_3Ga_5O_{12}$. The liquid phase epitaxy grown YIG exhibits exceptional interface quality, without an extended transient layer derived from interdiffusion processes of the substrate or impurity ions, thereby eliminating rare-earth impurity-related losses in the MI at low temperatures. At the TI-MI interface, high resolution depth-sensitive polarized neutron reflectometry confirmed the absence of a low-density transitional growth region of the TI. The demonstrated BT/YIG system is uniquely suited to elucidate the intrinsic TI-magnetic insulator magnetization dynamics due to the lack of an extended transient layer in the magnetic insulator at the magnetic insulator-substrate interface and lack of a low density, intergrowth region of the TI at the TI-magnetic insulator interface.

By overcoming these undesirable interfacial effects, we isolate and probe the intrinsic low-temperature magnetization dynamics and transport properties of the TI-MI interface. Using temperature dependent ferromagnetic resonance (FMR) we found a strong damping enhancement at low temperature due to the topologically protected Dirac surface states (TSS) in the Bi_2Te_3 film – a signature of significant spin pumping. Accompanying the damping enhancement, we also observed a large induced in-plane magnetic anisotropy for the BT/YIG heterostructure. We explain this by spin-pumping and spin-momentum locking, due to which the precessing spins of the YIG are forced to align with the spins pumped into the TSS and therefore remain locked in the plane of the BT/YIG interface. The temperature dependence of the magnetotransport which supports the suppression of bulk conduction, and the emergence of weak-antilocalization is consistent with the low temperature enhanced spin pumping in the BT/YIG that we observed, highlighting the interplay between the transport and spin pumping behavior in the TI-MI system. Further study of TI-magnetic insulator interfaces, specifically magnetic insulators with perpendicular magnetic anisotropy, are pertinent to potentially unlock high temperature quantum anomalous hall effect (QAHE) heterostructures, and the next generation of low power spintronics.

3:00pm **MI+2D+AC+TF-WeA-4 Falicov Student Award Finalist Talk: Surface Investigation of ε-phase Mn3Ga on GaN (0001) Substrate using Scanning Tunneling Microscopy***,* ***Ashok Shrestha***[3]*, A. Abbas, D. Ingram, A. Smith,* Ohio University

Antiferromagnetic materials have garnered significant attention due to their exotic properties and possible applications in next generation spintronic memory and computing devices [1]. In recent years, research on non-collinear antiferromagnetic materials such as Mn_3X (X: Ir, Ge, Sn, Ga) has heightened due to non-trivial, topological properties of these materials with unique spin textures [2]. Among these Mn-based antiferromagnets, Mn_3Ir has been commonly employed for applications [3]. As Ir is an expensive metal, efforts have been made to explore Ir-free antiferromagnets. Particularly, Mn_3Ga emerges as a promising candidate due to its versatile texture, magnetic ordering, and properties akin to Mn_3Ir [4]. Among the three distinct phases of Mn_3Ga, one of the most intriguing yet less explored is the ε-phase ($D0_{19}$-Mn_3Ga), which exhibits anomalous Hall effect and topological Hall effect in distinct temperature ranges [3]. In this presentation, we will delve into the growth and surface studies of a thin film of $D0_{19}$-Mn_3Ga on a Ga polar- GaN (0001) substrate.

We have successfully grown an epitaxial ε-phase Mn_3Ga layer using molecular beam epitaxy. The sample quality, lattice constants and crystal structure of the grown film were determined by *in-situ* reflection high energy electron diffraction and *ex-situ* X-ray diffraction. Upon examination with scanning tunneling microscopy, the surface revealed multiple terraces and row-like structures. Notably, the edges of the terraces form 120° angles with each other, consistent with the hexagonal crystal structure of the ε-phase Mn_3Ga. Additionally, we observed several stackings of just a monolayer, with their heights matching the c/2 value of Mn_3Ga. These measurements are further confirmed by X-ray diffraction. At atomic resolution, hexagonally arranged atoms with a 1 × 1 crystal structure were observed. The measured average *in-plane* atomic spacing was 5.37 ± 0.05 Å, deviating only -0.56% from theoretical predictions (5.40 Å). However, atomic spacing exhibited local variations. Other interesting structures were also observed in the scanning tunneling microscopy images, which will be discussed in the presentation. Chemical analysis via Rutherford backscattering confirmed the sample's Mn:Ga ratio as 3.2:1.0, which depends on the growth temperature. Further research will involve exploring non-collinear antiferromagnetism using spin-polarized scanning tunneling microscopy, with results to be presented at the conference.

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3:15pm **MI+2D+AC+TF-WeA-5 Thermally Generated Spin Transport Across Magnetic Interfaces***,* ***Hari Srikanth,*** USF Tampa **INVITED**

Spin-heat coupling and thermo-spin transport are topical areas of interest for the spintronics community. The origin of longitudinal Spin Seebeck effect (LSSE) and its relationship with magnetic anisotropy as well as magnon propagation across magnetic insulator/heavy metal interfaces have remained challenging issues. LSSE induces incoherent magnon excitations with the application of a temperature gradient across the thickness of a magnetic material. Although the ferrimagnetic insulator $Y_3Fe_5O_{12}$ (YIG) is known as the benchmark system for LSSE, other members of the insulating rare earth iron garnet family, *e.g.* the compensated ferrimagnet Gd_3Fe5O_{12} (GdIG), ferrimagnet insulator $Tm_3Fe_5O_{12}$ (TmIG) etc., are of interest and have received less attention from the point of view of spin-caloritronics. We have pioneered the technique of RF transverse susceptibility to probe the effective magnetic anisotropy in magnetic materials and heterostructures. Combining the RF transverse susceptibility with LSSE measurements, we have shown correlation between bulk and surface anisotropy with the field and temperature dependence of LSSE in YIG/Pt heterostructures and other compensated ferrimagnets like GdIG. Our recent work on TmIG/Pt heterostructures with varying film thickness reveals the clear role of anisotropy and Gilbert damping on the LSSE. From RF susceptibility, LSSE and broadband FMR experiments, quantitative analysis of the magnon propagation length and its correlation with magnetic anisotropy and Gilbert damping has been done. Overall, this talk would present new results in the thermal spin transport of garnet heterostructures which are of fundamental importance in spin transport across magnetic interfaces.

4:15pm **MI+2D+AC+TF-WeA-9 Spin Switchable 2D-Superlattice Metal-Halide Perovskite Film via Multiferroic Interface Coupling***,* ***Bogdan Dryzhakov,*** Oak Ridge National Laboratory*; B. Hu,* University of Tennessee Knoxville*; V. Lauter,* Oak Ridge Natinal Laboratory

Solution-processible 2D-phase metal-halide perovskites have emerged as a remarkable class of semiconducting, exhibiting a wide-range of optoelectronic properties and multi-functionalities. In this work, interfacing ferromagnetic spins with this semiconductor's Rashba band yields magnetic field control over the excited state spin degrees of freedom, as demonstrated through optical analogues that resolve the spin polarization in steady-state and dynamics, and in-situ neutron scattering methods, where a photo-ferromagnetic profile is depth-resolved. The 2D-superlattice perovskite films are prepared using an optimized, low-cost spin-cast method, resulting in highly crystalline and smooth thin films with a well-defined alternating layered structure of self-assembled organic cations and lead-iodide octahedra. Within the anisotropic 2D-planes of MHPs, fluorinated A-site ligands distort the lattice, yielding robust ferroelectricity and Rashba bands arising from broken inversion symmetry and strong spin-orbit coupling. Spin-switchable circularly polarized photoluminescence

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[1] **AVS National Student Award Finalist**

[2] **Falicov Student Award Finalist**

[3] **Falicov Student Award Finalist**

(CPL) between σ+ and σ- polarizations is achieved at the multiferroic perovskite/Co interface by manipulating the ferromagnetic spins on the Co surface between positive and negative magnetic field directions. This switching behavior arises from selective interactions between the ferromagnetic spins on the Co surface and the circularly polarized σ+ and σ- orbitals within the perovskite's Rashba band structures. Polarized neutron reflectometry measurements reveal long-range interactions of the Co magnetism to the perovskite's spin-polarized excitons, with chemical (NSLD) and magnetization (MSLD) depth profiles indicating optically induced magnetization through the perovskite's thickness. This work presents a fundamental platform for exploring spin selectivity effects within Rashba band structures using CPL studies in multiferroic perovskite/ferromagnetic interfaces.

4:30pm **MI+2D+AC+TF-WeA-10 Engineering the Hybrid Nanocolumnar Metamaterial Platforms for Advanced Optical and Magnetic Applications***, **Ufuk Kilic**, C. Briley,* University of Nebraska-Lincoln*; R. Feder,* Fraunhofer Institute for Microstructure of Materials and Systems, Germany*; D. Sekora,* University of Nebraska-Lincoln*; A. Ullah,* University of Nebraska - Lincoln*; A. Mock,* Weber State University*; C. Binek,* University of Nebraska - Lincoln*; H. Schmidt,* Friedrich Schiller University, Germany*; C. Argyropoulos,* The Pennsylvania State University*; E. Schubert, M. Schubert,* University of Nebraska - Lincoln

The hybrid metamaterial platforms have garnered remarkable attention in various subdiciplines of physics, chemisty, and biology due to their wide range of advanced functionalities including strong tunable optical and magnetic anisotropies, the ability to confine, modulate, and control of light, to engineer new permanent nanomagnets, for example. In this study, we employed a custom-built ultra-high vacuum electron-beam glancing angle deposition technique [1] to fabricate spatially-coherent, super lattice type nanocolumnar heterostructure metamaterial platforms from both hard (cobalt) and soft (permalloy) magnetic materials. Furthermore, by using atomic layer deposition technique, we incorporate ultrathin interface layer (~1.4 nm) of Al_2O_3 between the magnetic nano-columnar subsegments. This interface engineering at nanoscale provides another angle of freedom to tune both the magnetic and optical properties of hybrid nanocolumnar metamaterial platforms.

By taking the advantage of the generalized spectroscopic ellipsometry technique, we reached out the complex anisotropic dielectric properties of the fabricated structures. Our analysis involves widely used anisotropic Bruggeman effective medium model approach which provides to extract optical and structural properties, accordingly [2]. Moreover, to perform magnetic characterization of our fabricated metamaterial design, we employed both generalized vector magneto-optic ellipsometry and vibrating sample magnetometer measurements [3]. In order to delve into the fundamental driving mechanisms behind the anisotropic tunable magneto-optic responses from the proposed metamaterial platforms, we conducted a series of systematic micromagnetic and finite element modeling simulations, as well. We believe that these new structural metamaterial designs can result in the development of next-generation sensing devices, permenant nanomagnets, magnetic recording technologies, on-chip nanophotonic and opto-magnetic device applications.

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4:45pm **MI+2D+AC+TF-WeA-11 Magnetic Field Affects Oxygen Evolution Reaction Only in Metal Oxy-Hydroxides***, **Filippo Longo**,* Chemical Energy Carriers and Vehicle Systems Laboratory, Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland*; R. Peremadathil Pradeep, E. Darwin, H. Hug,* Magnetic and Functional Thin Films Laboratory, Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland*; A. Borgschulte,* Chemical Energy Carriers and Vehicle Systems Laboratory, Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland

Ni-based electrodes have been largely employed in alkaline electrolyzers for the production of H_2 and O_2 [1]. Due to the sluggish kinetics of the oxygen evolution reaction (OER), many experimental approaches have been employed to boost the catalytic performance of such electrodes [2]. The application of an external magnetic field during OER has shown outstanding catalytic improvement [3]. Despite considerable research effort, the understanding of its origin is still object of debate [4,5]. In this work we show how the Ni-based electrodes improve their catalytic activity towards OER during the application of an external magnetic field. We investigate in detail the catalytically active surface, the microscopic, electronic, and magnetic structures by soft- and hard X-ray photoelectron spectroscopy combined with impedance spectroscopy and magneto-optical measurements. It is relevant in this context that the oxy-hydroxide formed during OER is the catalytically active compound, and is thus likely also the origin of the magnetic effect. To underline the importance of the oxy-hydroxide formation, we employ a multilayered system made of Co-Pt-Ru multi-lattices, exhibiting much more favorable magnetic properties (such as strong perpendicular magnetic anisotropy) than nickel. Interestingly, hardly any improvement of OER is found. The various findings corroborate the picture of spin-exchange interaction of metal-oxide bonds as the underlying mechanism of the magneto-chemical effect.

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Thin Films
Room 115 - Session TF-WeA
Vapor Synthesis of Hybrid, Organic, and Polymeric Materials (VSHOP III)

Moderators: David Bergsman, University of Washington, **Rong Yang**, Cornell University

2:15pm **TF-WeA-1 Chemical Vapor Deposition of Polymers for Lithium Ion Batteries***, **Kenneth Lau**,* Rowan University **INVITED**

The lithium ion battery (LIB) technology is rapidly dominating the energy storage market due to its competitive cost and energy capacity. However, due to growing market demands, there is a continued push to enhance LIB energy and power density. As such, there is significant research into high capacity, high voltage cathode materials based on transition metal oxides that provide more lithium ion intercalation. However, at high voltages and high reactivity, the intercalation process becomes unstable and the transition metals tend to leach out into the electrolyte, leading to degrading battery performance with repeated charge-discharge cycling. Our work aims to protect and stabilize LIB cathode materials by conformally coating individual cathode particles with conducting polymers by oxidative chemical vapor deposition (oCVD). The hypothesis is that the protective conducting polymer helps to stabilize the cathode-electrolyte interface against degradation processes. In a second approach towards increasing LIB energy and power density, there is increasing research in moving away from 2D planar sandwich cells to pursuing 3D LIB architectures in which the electrodes are intentionally constructed into microstructured geometries (e.g. micropillars) to provide higher surface area and shorter lithium ion diffusion pathways. Our work aims to create 3D LIB anode microstructures through the carbonization of aromatic polymers grown by initiated chemical vapor deposition (iCVD). The hypothesis is that the simplified iCVD process scheme allows facile microstructural formation of polymer geometries that lead to viable microstructured carbon anodes. In this talk, we will highlight our recent work in using oCVD and iCVD to create polymers relevant for enhancing the performance of LIBs, particularly in improving capacity retention. We will present experimental correlations of how oCVD and iCVD processing chemistries and conditions impact material structure and device behavior, knowledge that has helped to understand the role of different dynamic processes, including adsorption, nucleation and growth kinetics.

2:45pm **TF-WeA-3 Exploring the Influence of Reduced Vacuum Conditions on Structural and Chemical Variations in Hybrid Perovskite Films Deposited by Resonant Infrared Matrix-Assisted Pulsed Laser Evaporation***, **Joshua Ayeni**, A. Stiff-Roberts,* Duke University

This study examines how gas kinetics impact the structural properties and chemical environment of phenylethylammonium lead iodide ($(PEA)_2PbI_4$) films deposited by resonant infrared matrix-assisted pulsed laser evaporation (RIR-MAPLE) under various background pressures (BGPs) of inert gas. $(PEA)_2PbI_4$ is a promising hybrid perovskite material for optoelectronic applications such as LEDs [1-2], yet less extensive research exists on vacuum deposition compared to solution deposition. RIR-MAPLE uses a low-energy Er:YAG laser at 2.94µm to reduce material degradation by resonant absorption of a host matrix [3]. Hybrid perovskite materials are typically grown under an active vacuum in RIR-MAPLE. Thus, understanding film deposition in a reduced vacuum with a BGP of inert gas is critical to determining industrial scalability.

Films were deposited from active vacuum (10^{-5} Torr) to 500 mTorr in a nitrogen atmosphere. Standard film characterization such as AFM, SEM, XRD, PL, and UV-Vis absorbance do not reveal significant changes in film properties with increasing BGP. X-ray photoelectron spectroscopy (XPS) was used to characterize the chemical composition of film surfaces. Pristine films show two characteristic Pb peaks from the spin-orbit splitting at ~138.0 eV for $4f_{7/2}$ and ~143 eV for $4f_{5/2}$, corresponding to a fully coordinated Pb^{2+}in the perovskite system. Variations in the binding energies (BEs) and elemental ratio are observed for different BGPs, implying different chemical environments for the Pb element. At high BGPs, peak splitting is observed for Pb 4f, I 3d, and C 1s. Also, the I/Pb ratio determined from XPS exhibits marked differences with BGP. For BGP below 250 mTorr, the decrease in the I/Pb ratio relative to the stoichiometric ratio suggests iodine vacancies [4]. Conversely, at higher BGPs, high iodine content indicates an iodine-rich phase is present in the films.

Therefore, this study will explore how BGP affects gas diffusion, adsorption kinetics, and nucleation processes to provide better insight into gas-phase kinetics and film growth mechanisms. By combining experimental results with theory to understand the role of BGP in compositional changes, better control of stoichiometry, purity, bonding, or doping by RIR-MAPLE could be enabled.

This work is supported by the National Science Foundation under Grant No. NSF CMMI-2227551.

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3:00pm **TF-WeA-4 Low Surface Energy for Tuning the Surface Repellency through Initiated Chemical Vapor Deposition***, **Syed Ibrahim Gnani Peer Mohamed**, G. Kaufman, D. Egbebunmi, M. Bavarian, J. Shield, C. Zuhlke, S. Nejati,* University of Nebraska Lincoln

Surface-wetting properties are crucial in various applications, such as microfluidics, water treatment, drag reduction, immersion cooling, degassing, and self-cleaning surfaces. For instance, traditional additive manufacturing techniques have been used to fabricate omniphobic surfaces, but concerns about durability and scalability remain. This study presents a novel approach to ultra-low surface tension repellency through a two-stage fabrication method, which integrates scalable techniques to restructure the surface and initiated chemical vapor deposition (iCVD). By applying this method to bulk aluminum, we achieved robust, hierarchal roughened surfaces that repel ultra-low surface tension liquids, including n-hexane ($ɣ$ = 18.2 mN/m). This approach offers flexibility in substrate material and shows promising results for scalability and durability. Surface and subsurface chemical analysis revealed the preservation of perfluoroalkyl side groups crucial for imparting superhydrophobic functionality. Wetting characteristic assessments highlighted the impact of hierarchal roughness on repellency, with the PTFE-co-PPFDA coating outperforming PPFDA for lower surface tension liquids. We present data on the coating at a high value of surface availability and note the transition in properties of the coated materials as a function of surface availability. Importantly, this study's findings have practical implications, providing insights into the design and fabrication of hierarchal roughened surfaces for ultra-low surface tension repellency, three different applications of these surfaces will be discussed for the very-low surface energy samples that show surface energy in the range of 12 mN/m.

3:15pm **TF-WeA-5 From iCVD Thin Films to 3D Aeropolymers for Biomedical Applications***, **Torge Hartig**, J. Paulsen, W. Reichstein, M. Hauck, J. Piehl,* Kiel University, Germany*; M. Taale,* Universität Heidelberg, Germany*; T. Strunskus,* Kiel University, Germany*; C. Selhuber-Unkel,* Universität Heidelberg, Germany*; G. Schnell,* University of Rostock, Germany*; A. Amin,* National Research Center, Giza, Egypt*; R. Adelung,* Kiel University, Germany*; B. Freedman,* Harvard University*; F. Schütt, F. Faupel, S. Schröder,* Kiel University, Germany

With rising requirements for functional polymer surfaces, wet chemical approaches meet their limits. Representing an all-dry technology initiated Chemical Vapor Deposition (iCVD) thin films are highlighted regarding conformal coating of nanoscale features, tailoring of chemical functional groups, as well as crosslinking via copolymerization. The conformal nature of the iCVD process is used in PFAS-free superhydrophobic coatings based on femtosecond-laser processed substrates.

To understand the impact of certain functional groups on the bio-interface-performance, tailored surface chemistry coatings as well as nanocomposite coatings are compared regarding applications for human fibroblasts and respiratory viruses.

Furthermore, the conformal nature of iCVD coatings is used to fabricate freestanding 3D thin film scaffolds. For this, sacrificial porous tetrapodal ZnO is coated and etched wet-chemically resulting in so-called aero-polymers of more than 99% empty space. The used aero-hydrogels have striking compressive properties that can be tailored by crosslinking ratios. The scaffolds mimic the extracellular matrix shape allowing the use in 3D cell culture for muscle cell applications. To include electrical conductivity in the aero-hydrogels multilayers of graphene and iCVD hydrogels are fabricated resulting in optimized cell interaction.

3:30pm **TF-WeA-6 Investigating PEDTT Thin Films: Comparing Synthesis Methods and Properties for Electronic Applications***, **Siamak Nejati**, S. Gnani Peer Mohamed, L. Okpaire, V. Medic, M. Bavarian,* University of Nebraska-Lincoln, USA

This study explores the properties and characteristics of poly(3,4-ethylenedithiathiophene) (PEDTT) thin films synthesized using oxidative molecular layer deposition (oMLD) and oxidative chemical vapor deposition (oCVD). The investigation focuses on conductivity, defect-free film formation, and the influence of structural variations on the overall properties of these films. PEDTT, notable for its solvent-free synthesis, is examined for its potential applications in electronic devices, drawing comparisons with poly(3,4-ethylenedioxythiophene) (PEDOT). A comparative analysis of the oMLD and oCVD techniques highlights their efficiency, scalability, and resultant film properties. oMLD offers precise, controlled layer-by-layer deposition, while oCVD provides versatility with the thermal decomposition of organic precursors. This study aims to elucidate the relationship between synthesis methods and thin film properties through detailed experimentation. A key aspect of this research is understanding the mechanisms governing PEDTT's electrical conductivity, examining molecular structure, doping levels, and processing parameters. The study also evaluates PEDTT's ability to form defect-free films, emphasizing factors influencing film uniformity and integrity. Structural differences between PEDTT and PEDOT, particularly the roles of sulfur and oxygen atoms, are analyzed to reveal their impact on electronic properties and chemical reactivity. Furthermore, the structural features of PEDTT, including steric repulsion and twisted conformations, are shown to affect its porosity and surface area, with implications for surface modifications and interfacial interactions. The research delves into the deposition processes, focusing on the flow dynamics and vapor pressure of the ethylenedithiathiophene (EDTT) precursor, to achieve a comprehensive understanding of thin film fabrication. This investigation provides valuable insights into the interplay between synthesis methods, molecular structure, and thin film properties of PEDTT-based materials. By uncovering the mechanisms behind conductivity, defect-free film formation, and structural characteristics, this research advances the field of electroactive polymers and their applications in emerging technologies.

4:15pm **TF-WeA-9 Exploring New Avenues Resulting from the Rational Process Design of Sequential Infiltration Synthesis***, **Nari Jeon**,* Chungnam National University, Republic of Korea **INVITED**

Sequential infiltration synthesis (SIS) has been demonstrated as a novel approach for fabricating inorganic–organic hybrid materials and inorganic porous materials, thereby offering precise control overnano- to microscale morphology. This method relies on the infiltration of vapor-phase precursors into a polymer matrix, followed by the reaction of these precursors with coreactants in the matrix. SIS-derived thin films and nanostructures show promise for applications in lithography, photovoltaics, tribology, and water remediation. Despite the continuous expansion of the material library prepared through SIS, a comprehensive understanding of the growth mechanism of SIS is limited. During SIS, precursor diffusion and reactions occur concurrently in the polymer matrix. SIS-derived thin films exhibit various compositional and structural complexities. This study investigates the complex relationship between the key physical/chemical phenomena governing the SIS process and the structural/compositional distribution of SIS-prepared films using *in situ* and *ex situ* characterization techniques. Moreover, it explores the potential of using organic coreactants in SIS as a new means of controlling the compositional distribution of inorganic–organic hybrid thin films and the pore morphology of inorganic porous thin films. Finally, future research directions are provided to help establish SIS as a mainstream technique in the fields of atomic layer deposition (ALD) and ALD-derived processing.

4:45pm **TF-WeA-11 Vapor Phase Infiltration of ZnO into Photo-Polymerizable Polyacrylates: Patterning and the Importance of Free Volume***, **Mark Losego,*** Georgia Tech*; L. Demelius,* Graz University of Technology, Austria*; A. Coclite,* University of Bari, Italy

Vapor phase infiltration (VPI) exposes polymers to inorganic vapors that sorb into the polymer to transform it into an organic-inorganic hybrid material with properties unique from its parent polymer. This talk will discuss our work investigating VPI of ZnO into photopolymerized polyacrylates. Photopolymerizable polymers are easily micropatterned with standard photolithography or advanced two-photon lithography processes. VPI offers a way to transform these micro-patterned polymeric structures into more functional hybrid materials or even fully inorganic structures upon combustive removal of the polymer. However, this transformation from polymer to hybrid to inorganic requires control and understanding of the inorganic loading during the VPI process. Here, we will show how the addition of “soft” acrylate segments containing ethoxylated chains can increase the free volume of these network polymers and permit greater VPI uptake of inorganic precursors, leading to more inorganic loading. The increased free volume of these polymers is confirmed with thermal expansion measurements. These more “flexible” polymer networks increase both the VPI kinetics and the total inorganic mass loading. In the compositional depth profiles, we can also detect a transition from a diffusion-limited process to a reaction limited process. We will also demonstrate the basic ability to photo-pattern these polyacrylates and then VPI the structures to make micro-patterned hybrid materials.

5:00pm **TF-WeA-12 Effect of Alumina Priming on Structural and Electrical Properties of Zno Nanostructures Synthesized via Vapor-Phase Infiltration Into Self-Assembled Block Copolymer Thin Films***, C. Nam, **Won-Il Lee**, A. Subramanian,* Stony Brook University/Brookhaven National Laboratory*; K. Kisslinger,* brookhaven National Laboratory*; N. Tiwale,* Brookhaven National Laboratory

Alumina priming is a technique that can improve the fidelity of the vapor-phase infiltration (VPI) of weakly reactive organometallic precursors into polymer templates, such as self-assembled block copolymer (BCP) thin films. The process begins with the infiltration of trimethylaluminum (TMA), a strong Lewis acid that can diffuse and bind to Lewis-basic groups within polymers. Upon exposure to water vapor, TMA forms molecular alumina terminated with hydroxyl groups. This priming step promotes subsequent infiltration of weakly reactive organometallic precursors of target inorganic materials by activating the polymer matrix. While alumina priming expands the range of inorganics applicable to VPI, the insulating properties of bulk alumina can negatively affect the electrical properties of the final inorganic nanostructures produced by VPI. In this study, we explore the impact of alumina priming on the structural and electrical properties of zinc oxide nanowires derived from the VPI of diethylzinc (DEZ) and water into self-assembled poly(styrene-block-methyl methacrylate) (PS-*b*-PMMA) BCP thin films. We demonstrate the ability to easily adjust the characteristic dimensions, chemical composition, and electrical conductivity of the resulting aluminum-doped ZnO (AZO) nanowires by varying the TMA exposure time during a single-cycle alumina priming. Increasing the TMA exposure duration enhances not only ZnO infiltration fidelity but also ZnO electrical conductivity with the minimized resistivity of 14.3 kΩ·cm with an Al concentration of 6.02 % at a TMA exposure time of 100 s. Simultaneously, the variation of the TMA exposure time provides control over the final AZO nanowire feature sizes with width and height in the ranges of 26 – 33 nm and 23 – 47 nm, respectively. These findings provide a guideline for controlling the composition, dimensions, and electrical properties of alumina-primed metal oxide nanostructures based on VPI in polymer templates.

5:15pm **TF-WeA-13 Spectroscopic Study of the Inorganic Structure in Pim-1/Metal Oxyhydroxide Hybrid Membranes Synthesized via Vapor Phase Infiltration***, **Benjamin Jean**, I. Slagle, F. Alamgir, M. Losego,* Georgia Tech

Polymers of intrinsic microporosity (PIMs) have well-defined microporosity that provide excellent chemical separation ability. However, the chemical stability of these polymers in organic solvents limit their use in organic separations. Vapor phase infiltration (VPI) can be used to transform PIM membranes into organic-inorganic hybrid membranes with superior chemical stability and separation performance. This talk will address our recent efforts to better understand the physicochemical structure of VPI-synthesized hybrid PIM-1 membranes and the importance of the inorganic’s network structure within the hybrid to affect the membrane’s chemical stability and separation performance. We use a combination of spectroscopic techniques including advanced X-ray absorption spectroscopies (XANES and EXAFS) to study the structure of inorganic clusters in VPI treated PIM-1 hybrid membranes. In PIM-1/ZnO_xH_y hybrids, XPS and FTIR show the inorganic structure is primarily a hydroxide structure. EXAFS indicates that these inorganics readily form several metal atom clusters as well. The degree of inorganic clustering can be controlled by processing conditions such as exposure time and number of cycles. The membrane solvent stability appears to be most influenced by the degree of clustering. For PIM-1/AlO_xH_y hybrid membranes, XPS and FTIR in conjunction with DFT calculations indicate that the final inorganic species is an oxyhydroxide species. Solid state NMR and XANES provide additional evidence that these aluminum hydroxide clusters network with each other into larger chains or sheets. The degree of inorganic clustering can be controlled by processing conditions such as exposure time and number of cycles. The membrane material properties such as membrane selectivity and solvent stability can be modified significantly based on the degree of clustering. This talk will discuss these finding and provide guidance for how to design these materials to achieve desired properties like solvent stability and membrane selectivity.

5:30pm **TF-WeA-14 Nanoporous TiO_2 Coating Designed by Swelling-Assisted Sequential Infiltration Synthesis (SIS) of Block Copolymer for Self-Cleaning Application***, **Khalil Omotosho**, D. Berman,* University of North Texas

Highly porous photoinduced self-cleaning coatings are pivotal across a broad range of applications like surfaces for optical coatings, solar panels, mirrors, etc. In this work, we described a new technique to design nanoporous photocatalytic self-cleaning TiO_2 coating with very high hydrophilicity. This coating was created by the swelling-assisted sequential infiltration synthesis (SIS) of a block copolymer template (PS75-b-P4VP25), followed by the elimination of the polymer via oxidative thermal annealing in a furnace at 450 oC for 4 h. The optimization of the infiltration process was realized with the quartz crystal microbalance (QCM), by estimating the mass of infiltrated precursor molecules as a function of the number of SIS cycles. SEM image show that the adopted swelling-assisted SIS approach is suitable for designing smooth uniform TiO_2 film with an interconnected network of pores. The films exhibited good crystallinity in the anatase phase. Hydrophilic property of the film was improved upon 1 h Ultraviolet (UV) exposure, leading to unmeasurable contact angle values upon contact with water droplets. The photocatalytic self-cleaning performance of the synthesized porous TiO_2 nanostructures were tested by measuring the photocatalytic degradation of methylene blue (MB). They displayed promising photocatalytic activity, with ~92% of the MB degraded after 180 min of UV irradiation, thus demonstrating comparable level of photoactivity with commercial anatase TiO_2 nanoparticles of the same quantity. This result highlights a new robust approach for designing hydrophilic self-cleaning coatings with controlled porosity and composition.

5:45pm **TF-WeA-15 Permanent Electric Polarization in Vapor Phase Deposited Polymer Thin Films***, **Stefan Schröder**, T. Hartig, L. Schwäke, T. Strunskus, F. Faupel,* Kiel University, Germany

Dielectric materials with a permanent electric polarization, i.e. electrets, have been attracting great interest in application fields such as sensors/transducers, catalysis, cell growth and microfluidics. The increasing demand for device miniaturization and new application pathways, e.g. in organic electronics, creates the need for high precision thin films of such materials. However, since polymers exhibit the best electret properties, the production of precise, high-quality polymer electret films with sufficient dielectric breakdown strength on large-area substrates is a challenge for conventional wet chemical approaches. In this work, we present the latest results on electret thin film fabrication via initiated chemical vapor deposition (iCVD). The iCVD process is a single-step, solvent-free polymer thin film fabrication process capable to grow precise films of high dielectric breakdown strength on large-area substrates as well as complex geometries. Due to the CVD-typical growth, the process can be integrated into existing microelectronics process lines and enables e.g. the use of electret films in complex micro-electromechanical systems (MEMS). The electronic structure, trap landscape as well as polarization response of the electret films can be tailored by the deposition parameters and (co-)monomer combinations. First principle calculations assist in the search for suitable monomers which yield effective electret properties. The fabricated films are tested in different transducer and sensor devices, where they can provide new pathways for next-generation devices.

6:00pm **TF-WeA-16 Using ALD to Alter the Biological Response of Cellulose Fabrics*, Li Zhang*,** *M. Losego,* Georgia Institute of Technology

Atomic layer deposition (ALD) of metal oxides onto fabrics has previously been shown to alter the biological response various microbes have with a textile. For example, ALD ZnO_x coatings have been shown to both accelerate bacterial growth ("feeds" the bacteria) at low coating thicknesses (< 3 nm) and kill the bacteria at higher thicknesses. In this study, we examine how ALD coatings can alter the enzymatic biodegradation of cotton fabrics. Specifically, we study how AlO_x ALD coatings affect the cellulase enzyme *Trichoderma viride's* abilityto hydrolyze and degrade cotton fabrics. ALD coatings of AlO_x are deposited using trimethyl aluminum (TMA) and H_2O with cycle counts varying from 1 – 750 cycles (~0.12-93 nm). It was found that as little as one ALD cycle of AlO_x could reduce the enzymatic degradation by as much as 5% over a period of 5 days. Deposition of 10 ALD cycles resulted in a further reduction of enzymatic degradation of around 8% over the same time period. However, additional layers of deposition, up to 750 cycles, did not significantly reduce the degradation rate further. To explain both the initial reduction in degradation and the plateauing in rate, the chemical and physical structures of the coated fabrics were studied with X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM). XPS indicates that after 3 days of enzymatic degradation the deposited alumina layer is etched away. This dissolution may be due to the alumina layer dissolving in the acetic acid buffer required for the enzyme or because the enzyme is hydrolyzing the surface glucose monomers bound to the alumina. In contrast, the alumina layer on the 10 cycle treated fabric remains intact throughout all 5 days of the enzymatic degradation. This indicates that, on the time-scale studied, ALD deposition of 10 or more cycles results in an alumina coating that is able to survive the enzymatic hydrolysis process resulting in this large disparity between the untreated, 1 cycle and 10 cycle samples. SEM images of the fabrics coated with more cycles indicate crack formation in the as-deposited state and after submerging the fabric in water for 2 days, the amount of cracks present increases significantly. In summary, the large difference in enzymatic degradation for low cycle count fabrics can be explained by the alumina layer surviving and the much smaller difference between higher cycle count treatments can be explained by the primary diffusion mechanism of the enzyme being through the cracks formed in the alumina layer, bypassing any changes in thickness of the alumina.

Electronic Materials and Photonics
Room 114 - Session EM+2D+AP+QS+TF-ThM

Epitaxy: Advances in Materials Integration and Devices

Moderators: Haozhe Wang, Duke University, **Jason Kawasaki**, University of Wisconsin - Madison

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 chiplets 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/acsphotonics.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 H2 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_2 etching to Ar annealing and the use of H_2 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_2 etch or Ar anneal was performed before the buffer layer (BL) growth while a growth interrupt in H_2 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^{-2}.

The H_2 etch and H_2 growth interrupt prevented BPDs from expanding under UV stress of 13kWcm^{-2} and it is believed that the H_2 treatment specifically inhibited this expansion. To confirm the role of H_2, we performed a growth using the same conditions as the H_2 etch/interrupt, however, an Ar anneal was used instead of a H_2 etch and the growth interrupt was conducted in an Ar atmosphere instead of H_2. The sample was UV stressed up to 1000 Wcm^{-2} and it was found that four BPD expanded from the substrate into the epilayer. For comparison, a sample grown with a double H_2 etch (before the buffer layer growth and drift layer) and a sample grown with a H_2 etch plus H_2 growth interrupt did not produce faulting at the same power density. This indicates that H_2 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_2 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^{-1}

to 900 cm^{-1} 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 um mask provides a larger shadowing effect in comparison to 200 um mask. This leads to a larger gradient in permittivity over a longer in-plane distance in the GPM: light with wavenumbers 650 cm^{-1} to 1400 cm^{-1} can be confined over an in-plane distance of 30 um. 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 β-Ga_2O_3**, ***Thaddeus Asel**, B. Noesges, J. Li, Y. Kim, A. Neal, S. Mou,* Air Force Research Laboratory, Materials and Manufacturing Directorate, USA

β-Ga_2O_3 has been of significant interest due to its high electric breakdown field, commercially available native substrate, and shallow n-type donors. However, β-Ga_2O_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, β-Ga_2O_3 growth must balance the incorporation of Ga with the desorption of a volatile suboxide species, Ga_2O where this suboxide is a limiting step when growing β-Ga_2O_3 via molecular beam epitaxy (MBE) with a traditional Ga source. Increased Ga_2O desorption causes the growth rate of β-Ga_2O_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 β-Ga_2O_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 cm2 /V·s while Ga-rich sample peaked at only 198 cm2 /V·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 2.0×10^{16} cm^{-3} compared to the O-rich sample that was measured to have an acceptor concentration of 3.0×10^{15}, and order of magnitude lower. This is possibly due to the formation of V_{Ga} during the Ga_2O 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 cm^2/Vs) and mobility decreased with increasing compensating acceptor concentration. Overall, these results indicate the importance of Ga:O ratios in β-Ga_2O_3 films grown via MBE with conventional Ga sources. These results demonstrate how improved electronical performance can be achieved in β-Ga_2O_3 by growing under O-rich conditions and limiting the formation of V_{Ga} due to suboxide desorption.

9:15am **EM+2D+AP+QS+TF-ThM-6 Advancing Single-Crystalline Oxide Membrane Growth via Molecular Beam Epitaxy**, ***Shivasheesh 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 $SrCa_2Al_2O_6$) 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 $SrTiO_3$ membranes, ranging from a few unit cells to several hundred nanometers in thickness, using an SrO sacrificial layer, and a solution-processed amorphous $SrCa_2Al_2O_6$sacrificial layer. Films grows in a layer-by-layer growth mode on a solution-processed amorphous $SrCa_2Al_2O_6$ whereas in a step-flow growth mode on SrO sacrificial layer. Films grown on 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 $SrTiO_3$ seed layers onto an amorphous 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 $SrTiO_3$ Membranes Using a Solution-Processed, Amorphous $SrCa_2Al_2O_6$ 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***[1], 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 metallorganic 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**, *J. Swarup,* ***James 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 Al_2O_3 from $Al(CH_3)_3$ (TMA) and H_2O 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,

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[1] **Medard W. Welch Award Winner**

$L'_2\text{Al}L''$"), and a different organic oxidizing compound ($R\text{O}_x$).We have 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_2O_3 using TMA and either $R\text{O}_x$ or H_2O 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_2O but not with $R\text{O}_x$.At either process temperature, we find no evidence for significant coverages of a long-lived intermediate from the reaction of $R\text{O}_x$. Growth from the heteroleptic Al precursor is similar to that observed with TMA—essentially stoichiometric Al_2O_3 is formed, and growth occurs readily with H_2O 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_2O_3 on metal surfaces of Cu and Co has been examined for evidence of interfacial oxidation.[1] While growth with either co-reactant (H_2O or $R\text{O}_x$) does not lead to the oxidation of the underlying Cu substrate, use of H_2O leads to the oxidation of Co, while use of $R\text{O}_x$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_2O_3 thin film could result in oxidation at the Al_2O_3|metal interface, a process that is strongly hindered in the case of $R\text{O}_x$ 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_2 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.[1] For example, in the microelectronics industry, an ALD film often needs to be grown only on the dielectric (often SiO_2) 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,[2] 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_2O_3 films, on SiO_2 versus Cu surfaces by using X-ray photoelectron spectroscopy (XPS) and temperature-programmed desorption (TPD). On SiO_2, 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_2 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. Merkx, W. M. M. Kessels, *Chem. Mater.* **2018**, *31*, 2-12.
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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_2 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_2O_3 and ZrO_2.Here we extend this technique to study the reaction between bis(ethylcyclopentadienyl)magnesium ($Mg(CpEt)_2$) 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 heterogenous surface reactions.

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_6) and disilane (Si_2H_6) as the reactants on aluminum oxide (Al_2O_3) 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_2O_3 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_6 and Si_2H_6 exposures (Figure 2). The WF_6 exposures produce a tensile stress of ~+2 N/m. This tensile stress is correlated with WF_6 reacting with SiF_2H^* sacrificial surface species to deposit WF_5^* surface species ($SiF_2H^* + WF_6(g)$ -> $WF_5^* + SiF_3H(g)$). The Si_2H_6 exposures then partially release the tensile stress with a stress change of ~-1 N/m. The Si_2H_6 exposures redeposit SiF_2H^* sacrificial surface species ($WF_5^* + Si_2H_6(g)$ -> $WSiF_2H^* + SiF_3H(g) + 2H_2(g)$).

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.

Thin Films
Room 115 - Session TF2+EM-ThM

Thin Films for Microelectronics I: BEOL

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

11:00am **TF2+EM-ThM-13 Inherently Selective Thermal Atomic Layer Deposition of Copper Metal Thin Films**, ***Charles Winter,*** Wayne State University **INVITED**

The continued miniaturization of microelectronics devices has created the need for new high-performance materials and appropriate nanoscale deposition processes. Atomic layer deposition (ALD) is a growth technique that affords Angstrom level control of film thicknesses and can give perfect conformal coverage in high aspect ratio nanoscale features. Copper (Cu) is a central interconnect metal and its growth by ALD remains a topic of significant interest. Many Cu ALD processes have been reported, but most are limited to lower temperatures (<200 °C) because of limited thermal stability of the Cu precursors. Herein, we will describe a new thermal Cu ALD process that employs bis(2,2,6,6-tetramethyl-3,5-heptanedionate)copper(II) ($Cu(thd)_2$) and nitrogen compounds as precursors. Cu metal film growth trials were conducted between 175 and 300 °C using $Cu(thd)_2$ and hydrazine on a variety of substrates, including Ru, Cu, TiN, SiO_2, Si with native oxide, and Si-H. Self-limited growth of Cu films on Ru substrates was demonstrated at 225 °C for both $Cu(thd)_2$ and hydrazine, with a growth rate of about 0.25 Å/cycle. An ALD window was observed for this process between about 225 and 275 °C. The characterization of the Cu films will be overviewed, including compositions, resistivities, and surface morphologies. Inherently selective growth of Cu metal films was observed on metal substrates such as Ru, Cu, and TiN. No growth occurred on insulating substrates such as Si-H and SiO_2. Inherently selective growth of Cu films by ALD on metal substrates offers many new opportunities for metallization.

11:30am **TF2+EM-ThM-15 Effect of Hydrogen Annealing on Grain Growth of Tungsten Films**, ***Seunghyun Park,*** School of Advanced Materials Science & Engineering, Sungkyunkwan University, Republic of Korea*; S. Kim,* Department of Semiconductor and Display Engineering, Sungkyunkwan University, Republic of Korea*; C. Park, H. Kim,* School of Advanced Materials Science & Engineering, Sungkyunkwan University, Republic of Korea

Tungsten (W) has been widely used for first level metallization in memory and logic devices due to its low electrical resistivity and high thermal stability. In addition, it can be easily deposited as an ultrathin film with high step coverage through chemical vapor deposition (CVD) or atomic layer deposition, rendering it suitable for complex device structures. However, the dimensional down-scaling of metal lines to less than 10−20 nm is accompanied by a simultaneous decrease in grain size, which results in an inevitable increase in the resistance due to enhanced surface and grain boundary scattering [1]. Therefore, one possible approach to maintain low resistivity of the ultrathin W film at small dimensions could be the introduction of additional thermal annealing that effectively increases the grain size while using a low temperature below 400 °C.

A couple of researchers observed abnormal grain growth of nickel and vanadium by introducing H_2 during the annealing process at high temperatures above 600 °C [2, 3]. Based on these findings, this presentation aims to explore the annealing of ultrathin W films in an H_2 environment at various temperatures (300−500 °C). To evaluate the effectiveness of H2 in increasing grain size, N_2 and high-pressure H_2 annealing were also introduced. The W film of 20 nm thickness was deposited using CVD on a SiO_2/Si substrate coated with a TiN adhesion layer. Grazing incidence X-ray diffraction measurements revealed that H_2 annealing at 1 bar resulted in an increased crystallite size, indicative of grain size, compared to N_2 annealing under all temperature conditions, which was accompanied by a decrease in resistivity. In addition, the increase in the H_2 pressure to 5 bar increased crystallite size further and reduced electrical resistivity accordingly.

[1] D. Gall, J. Appl. Phys. 127, 050901 (2020).

[2] T. Wagner et al., Int. J. Mater. Res. 93, 401−405 (2002).

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11:45am **TF2+EM-ThM-16 Textured Growth of Zinc Sulfide on Back-End-of-the-Line (BEOL) Compatible Substrates**, ***Claire Wu,*** University of Southern California*; M. Surendran,* Lawrence Berkeley National Laboratory*; P. Tzeng, C. Wu, X. Bao,* TSMC, Taiwan*; J. Ravichandran,* University of Southern California

Scaling of transistors has enabled continuous improvement in the performance of logic devices, especially with recent advances in materials engineering for transistors. However, there is a need to surpass the horizontal limitations in chip manufacturing and incorporate the vertical or third dimension. To enable monolithic three-dimensional (M3D) integration of high-performance logic, one needs to solve the fundamental challenge of low temperature (<400 °C) synthesis of high mobility n-type and p-type semiconductor thin films that can be utilized for fabrication of back-end-of-line (BEOL) compatible transistors.1 Transition metal oxides are promising n-type materials; however there is a lack of p-type materials that can meet the stringent synthesis conditions of BEOL manufacturing. Zinc sulfide (ZnS), a transparent wide band-gap semiconductor, has shown room temperature p-type conductivity when doped with copper and crystallizes below 400oC when grown by pulsed laser deposition (PLD).2, 3 Here, we report growth of crystalline thin films of ZnS by PLD on a variety of amorphous and polycrystalline surfaces including silicon nitride, (SixNy) thermal silicon dioxide, (SiO2), hafnium dioxide, (HfO2) and titanium nitride (TiN). High-resolution thin film X-ray diffraction shows texturing of ZnS on all three substrates. Crystalline quality was investigated using rocking curve measurements. Surface and interface quality was measured using X-ray reflectivity and atomic force microscopy measurements. Further work in characterizing the film quality through electrical measurements such as conductivity and capacitance shall be discussed. This work showcases the capability of thin film growth of a wide band-gap semiconductor in BEOL compatible conditions with technological applications in transistor manufacturing.

References:

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12:00pm **TF2+EM-ThM-17 Steep-Slope IGZO Transistor with an Ag/$Hf_{1-x}Zr_xO_2$ Atomic Threshold Switch***, **Junmo Park**, D. Eom, H. Kim, Y. Kim, H. Kim,* Sungkyunkwan University, Republic of Korea

Atomic threshold switch (ATS) exhibits abrupt switching characteristics due to the formation of electrochemical metallization filaments by the diffusion of Ag or Cu atoms towardsthe dielectric [1].Recently, it has been consideredfor integration with a field-effect transistor (FET) to build a steep-slope FET that overcomes the conventional subthreshold swing (SS) limit of 60 mV/dec [2]. Up to now, various FETs implemented with Si, transition-metal dichalcogenide, and oxide channels have been actively adopted for integration with ATS devices [3]. Particularly, the steep-slope FET built with an indium gallium zinc oxide (IGZO) transistor isattracting great attention because its fabrication temperature is low enough to meet thethermal requirements of a back-end-of line (BEOL) process [4]. However, it was demonstrated not through monolithic integration but through electrical wiring after fabrication of individual devices [5].

In this presentation, we suggest a novel BEOL-compatible steep-slope FET where an IGZO transistor is monolithically integrated with an Ag/$Hf_{1-x}Zr_xO_2$ (HZO) ATS at less than 400 °C. The IGZO and HZO films were deposited using sputtering at room temperature and atomic layer deposition at 200 °C, respectively.The Ag/HZO ATS is connected to the drain electrode of the IGZO FET in series. The SS of IGZO transistors was controlled by varying the composition of the HZO film, resulting achievement of SS muchless than 60mV/dec.Furthermore, we found that the HZO film with a Zr content (x) of ~25% led to a lower threshold voltage compared to the same thickness HfO_2 single-layerand did not require a high voltage electroforming process (initialization). The detailed electrical characterization results of individual ATS, FET, and integrated ATS-FET devices will be discussed along with the physical and chemical characterization results of the HZO and IGZO films.

This work was supported by the GRRC Program of Gyeonggi Province (GRRC Sungkyunkwan 2023-B01)

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Thin Films
Room 115 - Session TF+EM-ThA
Thin Films for Microelectronics II: Ferroelectrics, Dielectrics, and Semiconductors

Moderators: Elton Graugnard, Boise State University, **Christophe Vallee**, University at Albany

2:15pm **TF+EM-ThA-1 Atomic Scale Control of Ferroelectric $HfZrO_x$ Thin Films through Atomic Layer Modulation***, **Ngoc Le Trinh**, C. Nguyen,* Incheon National University, Viet Nam*; B. Gu, B. Lee,* Incheon National University, Republic of Korea*; K. Yang,* Seoul National University, Republic of Korea*; H. Kim, H. Kim,* Korea Electronics Technology Institute (KETI), Republic of Korea*; M. Park,* Seoul National University, Republic of Korea*; Y. Kang,* Incheon National University, Republic of Korea*; S. Kim,* Ulsan National Institute of Science & Technology, Republic of Korea*; H. Lee,* Incheon National University, Republic of Korea

Over the past few decades, atomic layer deposition (ALD) has become a key technique for the fabrication of multicomponent films in Si devices, such as 3D memory and logic devices. Conventionally, the formation of multilayers by supercycle method consisting of two or more ALD processes has been used, and the compositional ratio of the films could be controlled by cyclic ratio of two ALD processes. However, the supercycle method could not be applied to a few nanometers range in film thickness due to inconsistent surface reactions and low out-of-plane uniformity. Based on understanding of surface reactions mechanism in ALD, we have studied the concept of atomic layer modulation (ALM) for fabrication of the multicomponent thin film with atomic-scale control. The main key idea of ALM is that the compositional ratio is determined by the physical steric hindrance and the chemical reactivity of two precursors on the surface which can be predicted by theoretical calculations. We fabricated a $HfZrO_x$ multicomponent thin film with controllable dopant ratio using a Hf precursor, tetrakis(dimethylamido)-hafnium (TDMAH), and a Zr precursor, tetrakis(ethylmethylamido)-zirconium (TEMAZ). Due to the differences of steric hindrance and chemical reactivities, the stoichiometry of $HfZrO_x$ thin films is determined by the exposure sequence of precursors. Theoretical calculations were performed using Monte Carlo (MC) and density functional theory (DFT) to study physical and chemical reaction mechanisms. The theoretical results are consistent with the experiments analyzed by X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM). From the ferroelectric property analysis, the ALM $HfZrO_x$ films showed superior properties than the others prepared by conventional supercycle method, such as higher 2Pr values of 39.4 $\mu C/cm^2$, which is 2 times higher than in supercycle ALD $HfZrO_x$ film. By enabling precise stoichiometric control at atomic level, the ALM method not only extends the potential for fabricating multicomponent oxide materials but also enhances the quality of the deposited films.

2:30pm **TF+EM-ThA-2 Plasma-Enhanced Atomic Layer Deposition Based Ferroelectric Field Effect Transistors***, **Chinsung Park**, P. Ravindran,* Georgia Institute of Technology, USA*; D. Das,* National Institute of Technology, India*; P. Ravikumar,* Georgia Institute of Technology, USA, Uganda*; w. chern, S. Yu, A. Khan,* Georgia Institute of Technology, USA

This presentation investigates the electrical characteristics of ferroelectric material $Hf_{0.5}Zr_{0.5}O_2$ (HZO) when deposited on Si using either thermal ALD or plasma ALD methods. Previous research has explored the differences in ALD deposition methods in metal-insulator-metal (MIM) capacitor structures with HZO deposited on metal. However, considering emerging non-volatile memory (eNVM) applications, a comparative evaluation based on Si substrates is necessary but has not yet been reported. We examined how the characteristics differ between thermal and plasma ALD deposition methods in metal-oxide-semiconductor (MOS) structures compared to MIM structures. Experiments were conducted by fabricating ferroelectric field-effect transistors (FEFETs) using thermal and plasma ALD deposition methods, followed by electrical characterization. The results showed that devices fabricated using plasma ALD exhibited similar results to MIM structures in MOS structures, including no wake-up effect, better endurance (one order higher), and a larger coercive voltage (V_c). Additionally, HR-TEM cross-sectional analysis revealed that plasma ALD requires a larger write voltage to achieve a given memory window due to the presence of a thicker SiO_2 interfacial layer. Through this study, it was observed that ferroelectric HZO devices fabricated using thermal ALD require wake-up and have one order lower endurance but offer the advantage of lower write voltage. On the other hand, devices fabricated using plasma ALD exhibit no wake-up effect, better endurance (one order higher), but have higher write voltage. Considering these characteristics, future device designs may benefit from taking into account the differences in characteristics based on ALD methods.

2:45pm **TF+EM-ThA-3 Effect of Annealing Temperature on the Electrical Characteristics of $Hf_{0.5}Zr_{0.5}O_2$/InGaZnO Ferroelectric Field-Effect Transistor***, **Deokjoon Eom**, H. Kim, W. Lee, J. Lee, C. Park, J. Park, H. Lee, Y. Kim, H. Kim,* Sungkyunkwan University (SKKU), Republic of Korea

Recently, amorphous-oxide-semiconductor (AOS) materials, such as InGaZnO (IGZO), InZnO, and InWO, have been widely studied as channel materials for ferroelectric field-effect transistors (FeFETs) with a $Hf_{0.5}Zr_{0.5}O_2$ (HZO) gate dielectric because of their superior interface properties compared to Si channel-based FeFETs [1]. Typically, the fabrication of bottom-gate FeFETs with an AOS channel requires post-deposition annealing (PDA) after channel formation, which induces the formation of the ferroelectric orthorhombic phase in the HZO film and activates the AOS channel layer [2]. Meanwhile, it was reported that hydrogen atoms incorporated within the high-k film during atomic layer deposition (ALD) diffuse towards the IGZO channel region under thermal annealing, resulting in a notable change in the transfer characteristics of AOS-based FETs [3]. However, there is still a lack of research observing the detailed changes in the chemical and electrical properties of AOS-based FeFETs as a function of the PDA temperature.

In this presentation, we study the effect of PDA temperature on the electrical properties of bottom-gate HZO/IGZO FeFETs, where the PDA temperature was varied from 300 ℃ to 600 ℃ using rapid thermal annealing. The HZO and IGZO films were deposited in series via ALD with a Hf:Zr cycle ratio of 1:1 and sputtering of an IGZO target (In:Ga:Zn=1:1:1), respectively. Microstructural analysis revealed that, despite a significant volume shrinkage, the IGZO film maintained its amorphous structure after PDA at 600 °C, while the ferroelectric phase emerged in the HZO films after PDA at 400−600 ℃. Distinct changes in hydrogen content within the IGZO/HZO stack were observed at different PDA temperatures. These changes in hydrogen content, along with the evolution of the ferroelectric phase, significantly influenced the transfer characteristics of the fabricated devices, including parameters such as the threshold voltage and hysteresis loop direction.

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3:00pm **TF+EM-ThA-4 Polarization Switching in Metal-Organic MBE-Grown Metal-Ferroelectric-Metal Heterostructures***, **Anusha Kamath Manjeshwar**, Z. Yang,* University of Minnesota*; A. Rao, G. Rojas,* University of Minnesota, USA*; J. Wen,* University of Minnesota*; C. Liao, S. Koester, R. James, B. Jalan,* University of Minnesota, USA

Metal-ferroelectric-metal heterostructures have diverse applications ranging from ferroelectric non-volatile memories and sensing to neuromorphic computing. Traditionally, lead-based perovskite oxide ferroelectrics such as PZT and PMN-PT have been leading contenders in some of these applications. However, the toxicity of lead has prompted a renewed interest in the latent potential of lead-free ferroelectrics such as $BaTiO_3$ within the perovskite oxide family.

A long-standing challenge to unlock the potential of $BaTiO_3$ is systematically isolating the effect of parameters such as epitaxial strain, stoichiometry, and dimensionality on the ferroelectric properties of $BaTiO_3$ films. Producing reliable thin-film metal-ferroelectric-metal heterostructures for these studies depends on the (1) degree of control in the synthesis of each layer and (2) the atomic sharpness of the metal-ferroelectric interfaces. Despite molecular beam epitaxy (MBE) being the preferred growth method for heterostructures due to the high quality of the constituent layers and abrupt interfaces, the growth of ferroelectric $BaTiO_3$ with $SrRuO_3$ as metallic electrodes has two key challenges. First, elemental Ru is simultaneously difficult to evaporate and oxidize, requiring the use of electron-beam evaporators and potent oxidants which complicate stoichiometry control. Second, balancing the retention of molecular flow and preserving ideal oxygen stoichiometry and, consequently, ferroelectricity restricts the oxygen background pressures to ~1-3 orders of magnitude lower than in other synthesis methods.

We present the growth of $SrRuO_3$ and $BaTiO_3$- films using metal-organic MBE, overcoming both challenges. Using a solid metal-organic precursor for

Ru, we show the presence of an adsorption-controlled growth window within which the films self-regulate their cation stoichiometry for $SrRuO_3$ films on $SrTiO_3$ (001) substrates. We grow phase-pure, epitaxial, single-crystalline $BaTiO_3$ on $SrRuO_3$-buffered $SrTiO_3$ (001) substrates and note polarization switching with piezoresponse force microscopy for an applied bias of ± 6 V for a ~36 nm $BaTiO_3$ film without any post-growth oxygen annealing. We extend this technique to grow $SrRuO_3/BaTiO_3/SrRuO_3$ heterostructures on Nb-doped $SrTiO_3$ (001) substrates. For a ~40 nm $BaTiO_3$ layer, we observe a room-temperature static dielectric constant of ~400 and ideal capacitor-like behavior up to 1 kHz using impedance spectroscopy. We demonstrate hysteretic *P-E* curves with $P_r \sim 17\ \mu C\ cm^{-2}$ and an $E_c \sim 221\ kV\ cm^{-1}$ at $f = 1$ kHz. We will discuss the effect of stoichiometry, strain, and dimensionality on the structural and dielectric properties of metal-organic MBE-grown $BaTiO_3$.

3:15pm **TF+EM-ThA-5 Integration of Barium Titanate onto high-Al content AlGaN***, **Peter Dickens**, A. Allerman, C. Harris, B. Klein,* Sandia National Laboratories

Wide-bandgap transistor development for next generation power electronics is promising. This is due to their higher breakdown field and saturated electron velocity over traditional silicon insulated-gate bipolar-transistors, and within this development, a push towards wider bandgaps in the $Al_xGa_{1-x}N$ system by increasing the Al-content is desired to further improve breakdown strengths and power densities in devices.However, even with higher breakdown strength, electric field spikes between the gate-drain on high-electron-mobility-transistors can result in device failure far below the inherent breakdown strength of the semiconductor.This has led to the integration of high-permittivity dielectrics on top of the semiconductor to mitigate these spikes; $BaTiO_3$ has received much of the attention owing to its large dielectric constant.Here we will report on the integration of RF sputtered $BaTiO_3$ thin films onto $Al_{0.85}Ga_{0.15}N$ substrates with a focus on the film morphology under specific deposition conditions.Results will focus on film morphology (x-ray diffraction, scanning electron microscopy, and atomic force microscopy) and stoichiometry (electron microprobe and x-ray fluorescence).

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3:30pm **TF+EM-ThA-6 Understanding the Crystallization of $BaTiO_3$ Thin Films Prepared by Atomic Layer Deposition***, **Jiayi Chen**,* Georgia Institute of Technology, USA, China*; A. Khan, M. Losego,* Georgia Institute of Technology, USA

This talk will discuss our work to develop a robust atomic layer deposition process (ALD) to create ferroelectric $BaTiO_3$ thin films.Ferroelectric materials are the potential candidates for future low voltage RAM and NAND memory because of their reversible two polarization states under low external electric field. While the CMOS compatible gate dielectric materials HfO_2 and $Hf_{0.5}Zr_{0.5}O_2$ are ferroelectric, they have high coercive fields which makes it difficult to lower switching voltages to below 1V. Therefore, perovskite ferroelectric materials, like $BaTiO_3$ are desirable to use for these applications because their coercive voltages can be an order of magnitude lower, approaching 0.1 V.However, such a ferroelectric needs to be deposited by ALD to match the conformality and small thickness requirements desired for RAM and NAND memory and unfortunately, the deposition of multicomponent, stoichiometric crystalline phases by ALD is extremely challenging.In this talk we will discuss our efforts to achieve ALD of $BaTiO_3$ and discuss its microstructure, chemistry, and electrical properties.Specifically we will discuss variations caused by the use of different titanium precursors and their potential to lead to reduced oxidation states, hydrated phases, or carbon contamination that can prevent crystallization.We will also discuss the influence of these chemistries on stoichiometry and the ability to get pure crystalline phases.

3:45pm **TF+EM-ThA-7 Thermal and Plasma ALD BN for Low-k Applications***, **Pegah Bagheri**, M. Konh, R. Pearlstein, X. Lei, H. Chandra,* EMD Electronics, USA

Integration of low dielectric constant thin films in transistors and memories is a crucial step in realization of high speed, low-power and high-performance switches with lower parasite capacitance. Dielectric films, such as SiO_2 and Si_3N_4 and amorphous films deposited via Atomic Layer Deposition (ALD), were studied extensively providing a wide range of dielectric constants from 4.0 to 7.0. However, next generation of low-K spacer films targeting low-power high-performance applications requires conformal films on patterned structures with dielectric constant below silicon oxide (< 4.0) with good leakage current as low as $<10^{-7}\ A.cm^2$ at 1 MV/cm. Moreover, these thin films are expected to show high stability and high resistance to etching after exposure to HF which are typical integration steps in semiconductor device processing. Boron nitride is a new materials system in which lower dielectric constant than SiO_2 and Si_3N_4 is expected.-Previous study demonstrated PECVD boron nitride films with k as low as 2.0. Deposition of amorphous BN via ALD seems to be a superb candidate for the next generation of low-K spacer materials with dielectric constant below 3.0.

In this work, BN deposition was studied by use of BCl_3 and NH_3 as Boron and Nitrogen sources. NH_3 reacted with BCl_3 via surface-controlled reactions both thermally at 300°C, 400°C and 500°C and through NH_3 plasma generation at 200W and 300°C. ALD-deposited BN films showed uniformity of below 5% and thickness of 200Å measured by ellipsometer. Furthermore, electrical performance of BN films was measured by Capacitance-Voltage and Current-Voltage in Metal-Insulator-Semiconductor (MIS) structure using Mercury probe. To understand the incorporation of B and N and other elements such as C, O and Cl, crystallinity degree of the films and B-N bonding structures, X-ray Photoelectron Spectroscopy (XPS) and Fourier Transform Infrared Spectroscopy (FTIR) were utilized. Finally, the stability and resistance of ALD BN films to HF exposure was measured and monitored with time.

It was shown that amorphization degree increases at lower temperature and use of NH_3 plasma. However, thermally deposited BN at lower temperature showed high oxygen incorporation leading to degraded properties such as instability, low resistance to etching and poor electrical performances. Plasma ALD BN showed the lowest dielectric constant at 3.4 and wet etch rate below 0.03 time of the thermal oxide. Nevertheless, all BN films deposited with BCl_3 and NH_3 resulted in B/N~1.3 indicative of poor network formation. This led to formation of instable films with rough surfaces and degradation of bulk properties overtime.

4:00pm **TF+EM-ThA-8 Quantum Chemical Analysis for Effects of Carbon and/or Nitrogen Bond-Types on Dielectric Constant and Leakage Current in Low-K Dielectric SiOCN Film***, **Hu Li**, J. Zhao, P. Ventzek,* Tokyo Electron America, Inc.

Silicon Oxycarbon nitride (SiOCN) films are promising low dielectric(low-*k*) materials in semiconductor devices. The SiOCN film is fabricated using various fabrication technologies, that is, atomic layer deposition (ALD) and chemical vapor deposition (CVD), for specific applications such as inner spacers, gate spacers, and bottom contact etch stop layers (BCESL) in the deposition processes. Film deposition requires atomically precise control, with an increasing demand for nanoscale multilayer architectures. To further develop the SiOCN film properties and deposition processes, precise control of the bond-types in the fabrication process is required to maintain a low-k film property without increasing the risk of leakage current and/or decreasing the film density, particularly in a plasma enhanced ALD (PEALD) process. Chemically reactive species, such as radicals and energetic ions, generated in the plasma easily affect the film properties during plasma treatment by modifying the bond-types or surface structures. However, neither the effects of the reactive species on the formation of specific bond-types nor the effects of these bond types on the film properties are fully understood. Therefore, in this study, we examined the effects of various -Si-M-Si- bond-types ($M=C_xN_yH_z$) on the dielectric constant and leakage current using quantum chemical simulation. Our simulation modeling is based on experimental observations (XPS and FTIR). We found that when a carbon atom was present in a film with dangling bonds strongly affects the *k* values. The simulation results also showed that the Si-C-Si bond formed a mid-gap state, resulting in leakage current. When a carbon atom exists in the form of $Si\text{-}CH_2\text{-}Si$, no mid-gap state was observed, and such bond-type lowers the k value of the film. These results suggest that hydrogen plasma treatment may effectively prevent leakage current and yield low-k film structures. The effects of other bond-types and their concentrations on the k values and leakage currentare discussed in this presentation.

4:15pm **TF+EM-ThA-9 Electrical Measurement of in-situ Boron-Doped Epitaxial $Si_{1-x}Ge_x$ Films with Crystalline Defects***, **Hyung Chul Shin**, D. Eom,* Sungkyunkwan University (SKKU), Republic of Korea*; D. Yoon,* Yonsei University, Republic of Korea*; K. Kim, H. Yoo,* Samsung Electronics Co., Republic of Korea*; D. Ko,* Yonsei University, Republic of Korea*; H. Kim,* Sungkyunkwan University (SKKU), Republic of Korea

Since its introduction as a channel-strain inducer in the early 2000s [1], in-situ epitaxial $Si_{1-x}Ge_x$ films doped with boron (B) have been continuously employed as source and drain (S/D) regions in high-performance p-channel transistors, including the most advanced devices with a gate-all-around structure [2]. However, when the B doping concentration exceeds 10^{21} atoms/cm^3 in the $Si_{1-x}Ge_x$ film, the B atoms may partially occupy interstitial sites or form clusters, producing defects that can reduce the electrical activation ratio [3]. Therefore, it is crucial to assess these defects through electrical characterization because they can significantly impact the final device performance [4]. Furthermore, while the effect of defects on the electrical properties of $Si_{1-x}Ge_x$/Si p^+−n diode has been studied in the context of their application to S/D regions [5], there remains a need for a more extensive study, including further investigation of their effect on the contact properties of $Si_{1-x}Ge_x$ to the overlaid metals.

This presentation discusses various electrical properties of in-situ B-doped $Si_{1-x}Ge_x$ films epitaxially grown on n-type Si substrates, where crystalline defects are intentionally induced by varying the thickness and doping concentration. Various electrical parameters, such as reverse leakage current, on/off ratio, ideality factor, and activation energy, were extracted from the current−voltage characteristics of the p^+−n diodes. These parameters' changes were correlated with the presence of defects in the $Si_{1-x}Ge_x$ film. In addition, the contact resistivity values measured by a circular transmission line method also exhibited a similar trend, demonstrating reliable results regarding the effect of these defects.

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Thin Films
Room Central Exhibit Hall - Session TF-ThP
Thin Films Poster Session

TF-ThP-1 Enhancing The Performance of Amorphous IGZO Thin-Film Transistors Via Oxygen Plasma Treatment*, **Jae-Yun Lee**, A. Tukhtaev, J. Berdied, X. Wang, H. Zhao, S. Kim,* Chungbuk National University, Republic of Korea

In this work we present significant improvement in the electrical characteristics of a 50 nm-thick a-IGZO layer deposited by radio-frequency (RF) sputtering after employing oxygen plasma treatment. After formation, the active layer was thermally annealed at 300 °C for 1 hour before beginning the oxygen plasma treatment. The effects of the plasma generator RF power were studied at 60, 120 and 180 W. The oxygen plasma was found to affect the optical absorption, surface roughness and the atomic composition of the thin film as well as the device performance of the TFTs based on the a-IGZO layers. The on/off current ratio and subthreshold swing improved significantly after the treatment compared to the device with the as-deposited a-IGZO layer. For the charge carrier mobility and threshold voltage however, the devices treated with oxygen plasma generated at 60 W showed the best performance, and both parameters have deteriorated at higher RF powers. Interestingly, at 180 W the mobility was reduced to and the threshold voltage increased over than that of the device with the as-deposited a-IGZO. The X-ray photoelectron spectra of the thin films were analyzed. It was found that the a-IGZO treated with oxygen plasma at 60 W RF power has the lowest ratio of OH groups which are often related to charge trapping in metal-oxide semiconductors. The optical band gap, as extracted from the Tauc plot, is the highest of this thin film, further suggesting decreased trap density, confirming the effect of traps on device performance. The atomic force microscope imaging showed that the surface roughness significantly decreases after the plasma treatment. This might explain the sharp improvement in the subthreshold swing, which is influenced by surface-related charge trapping. This study shows that the post-deposition oxygen plasma treatment of RF sputtering-deposited a-IGZO active layer is an effective way to enhance TFT performance by inducing favorable changes in the physical properties of the metal-oxide film.

Acknowledgements

This research was partly supported by Innovative Human Resource Development for Local Intellectualization program through the Institute of Information & Communications Technology Planning & Evaluation (IITP) grant funded by the Korea government (MSIT) IITP-2024-2020-0-01462 (34%), in part by the Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by Ministry of Education under Grant 2020R1A6A1A12047945 (33%), and in part by the Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education under Grant RS-2023-00249610 (33%).

TF-ThP-2 Surface Analysis of Nanolayers by LEIS, SIMS and XPS*, B. Hagenhoff,* Tascon GmbH, Germany*; J. Tröger,* University of Münster, Germany*; **Elke Tallarek**, D. Heller-Krippendorf,* Tascon GmbH, Germany

Advanced and smart materials nowadays consist of various materials featuring layers and layer systems at the nanoscale. In order to monitor the development process as well as production and customer returns, analytical techniques are required which have an information depth suited for the layered samples.

Starting with information from the outermost atomic layer using Low Energy Ion Scattering (LEIS), adding Time-of-Flight SIMS (ToF-SIMS) for the outermost 3-5 monolayers and ending with X-ray Photoelectron Spectroscopy (XPS) for accessing up to 20 monolayers, a detailed insight can be gained into the composition of layers at the nanoscale. On the other hand, layer systems the structure of which is well known can help to better understand the performance features of the different analytical techniques.

In our ongoing studies we have compared analytical results from LEIS, ToF-SIMS and XPS for various layered systems. We will report on films produced by Atomic Layer Deposition (ALD) as well as core-shell nanoparticles. Amongst the three, XPS is the most often used technique in industry because of its power to obtain quantitative results. Our comparative data will help to put XPS data in a suited information depth perspective.

TF-ThP-3 Role of Solvent Treatment on the Structure and Thermoelectric Properties of oCVD PEDOT Films*, **Ramsay Nuwayhid**, T. Novak, B. Jugdersuren, X. Liu, J. Long, D. Rolison,* U.S. Naval Research Laboratory

Vapor-phase routes to organic conducting polymers offer many advantages over more commonly studied solution-phase methods. Conductive polymers often require functionalization to be soluble in an appropriate solvent, and techniques such as spin-coating or drop-casting are generally only suitable for relatively flat substrates. Oxidative chemical vapor deposition (oCVD) is an alternative that allows for precise control of coatings over complex 3D substrates. oCVD can produce highly conductive conjugated polymer films, notably PEDOT, but compared to solution-phase PEDOT(:PSS) films, there has been little research into optimization of these films for thermoelectric applications. In this work, we demonstrate that post-deposition treatments with common organic solvents, such as dimethyl formamide (DMF), ethylene glycol (EG), or dimethyl sulfoxide (DMSO), significantly improve the Seebeck coefficient and resulting power factor for oCVD-grown PEDOT films. Given the lack of PSS in oCVD-grown films, much of the enhancement observed in spin-coated films after solvent treatments cannot be related to removal/segregation of the PSS phase, which is a common assertion. Despite this lack of PSS, we observe Raman changes very similar to those previously seen in PEDOT:PSS films, including the disappearance of peaks previously assigned to PSS. For oCVD-grown PEDOT, we find significantly reduced Cl content after solvent treatments, which likely de-dopes the PEDOT films and subsequently enhances the Seebeck coefficient. These results not only show solvent-treatments to be effective in improving the thermoelectric properties of oCVD-grown films, but also prove that many of the phenomena attributed to PSS in spin-coated films may be related to other chemical or structural changes in the PEDOT chain.

TF-ThP-4 Development of Low-K/ High-K Multilayers for Power Capacitors*, **Julie Chaussard**, H. Houmsi, C. Guérin, A. Lefèvre,* CEA-Leti, France*; P. Gonon,* LTM-CNRS, France*; V. Jousseaume,* CEA-Leti, France

Power electronics gather many emerging applications such as electrification of transports. In power devices, voltage fluctuations can occur and damage GaN transistors, especially during switching phases. To prevent this, a snubber network can be used. It consists of a series capacitor and resistor connected in parallel to a transistor. Capacitor must have high capacitance, high breakdown voltage and thermal stability up to 150°C (operating temperature for electric vehicles). Furthermore, capacitor and resistor are usually surface-mounted devices and have disadvantages of low heat dissipation and large size. One way to miniaturize these passive components would consist in 3D integration on silicon wafers.

Today, polymer capacitors are widely used because of their low-cost manufacturing and high electric breakdown strength. However, thin films of polymer cannot be conformaly deposited into 3D structures. Also, most of polymers have low operating temperature, lower than the 150°C targeted. Among alternative non-polymeric materials, two groups stand out: high-k (with high dielectric constant but low breakdown voltage (V_{bd})) and low-k materials (higher V_{bd} than high-K materials). A strategy has to be developed to find a compromise between high dielectric constant and high breakdown voltage. A promising way is to integrate high-k/low-k multilayers into a MIM (=Metal-Insulator-Metal) capacitor.

In this work, multilayers combining an organosilicate (SiOCH) as low-k and HfO_2 as high-k were investigated. SiOCH thin films were deposited by plasma-enhanced chemical vapour deposition while HfO_2 thin films were deposited by atomic layer deposition. Chemical and physical properties of the films were studied using FTIR, ellipsometry, X-ray reflectometry and X-ray diffraction. Then, different thicknesses and stacks were fully integrated into MIM capacitors on 200 mm Si wafers for electrical characterizations. Electrical parameters such as dielectric permittivity, dielectric losses, leakage current and breakdown field were measured. It is shown that the introduction of very thin HfO_2 layer (in the 10 nm range) between SiOCH layers (50 nm thick) allow to increase the dielectric constant up to 11%. The use of more complex stack (i.e. up to 5 layers) further improves the C^*V_{bd} parameter. This approach combining low-k and high-k looks promising for the realization of high-voltage 3D capacitors on Si.

TF-ThP-5 The Electrical, Sensory and Photocatalytic Properties of Graphene Oxide and Polyimide Implanted by Low and Medium Energy Gold Ions*, **Josef Novák**,* Nuclear Physics Institute of the CAS, Czechia

In our work, we focused on the investigation of the electrical, photocatalytic and sensory properties of graphene oxide (GO) and polyimide (PI) implanted by gold energetic ions. Gold ions (Au^+) are favored for ion implantation into polymers due to several key reasons. Primarily, Au^+

possesses exceptional electrical conductivity, rendering it highly suitable for establishing conductive pathways within the polymer matrix. Additionally, gold exhibits remarkable chemical stability, thereby minimizing undesired reactions with the polymer substrate during the implantation process. The implantation of Au^+ ions is accompanied by crystallization and carbonization of the modified samples, which leads to the disruption of chemical bonds and the formation of network processes [1].]. These processes lead to the formation of conjugated systems that promote electric charge transport [2].

The organic non-conductive materials (GO, PI) were subjected to modification using low-energy Au^+ ions (20 keV) and medium-energy Au^+ ions (1.5 MeV). The ion implantation was conducted with three different ion fluences. At the lowest ion fluence (3.75×10^{12} cm^{-2}), the formation of carbon islands may occur. The second ion fluence (3.75×10^{14} cm^{-2}) induces the growth of carbon clusters and the formation of conjugated carbon bonds [2]. With the highest ion fluence used (1×10^{16} cm^{-2}), the formation of metal nanoparticles is expected to take place [3].

The experimental research has been carried out at the CANAM (Centre of Accelerators and Nuclear Analytical Methods) infrastructure LM 2015056. This publication was supported by OP RDE, MEYS Czech Republic under the project CANAM OP CZ.02.1.01/0.0/0.0/16 013/0001812. The scientific results were obtained with the support of the; GACR Project No. 23-06702S and University of J. E. Purkyne student project UJEP-SGS-2023-53-007-2.

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TF-ThP-6 HfO$_2$ Thin Film for Si and SiC MOS Capacitor

Rodrigo Reigota Cesar, Center for Electronic Components and Nanotechnology - CCSNano, Brazil

Silicon carbide (SiC) began to be studied in the late 1980s. Initially used as an abrasive material in cutting tools, it has become a highly promising material in the microelectronics industry due to its properties such as high thermal conductivity, high breakdown voltage, high mechanical hardness, large band gap, good chemical stability, high electron saturation velocity, and high thermal conductivity. Therefore, it is ideal for developing devices used in extreme conditions of power and/or temperature. It is widely used in the aerospace industry, in satellites, and nuclear reactors.

Another crucial aspect in the process of manufacturing devices with SiC substrate is surface passivation. This process completes the open bonds of carbon ions, thereby reducing surface defects and charge density. Various passivation methods exist, including oxidation, nitridation, doping with phosphorus ions, and treatment in a furnace with N2+O2 gas, with the latter being the most commonly used. In addition to these methods, another way to help reduce surface charge density in the final device is to utilize high-k dielectrics, such as aluminum oxide (Al2O3), titanium oxide (TiO2), hafnium oxide (HfO2), or even aluminum nitride (AlN). In this context, the aim of this work is to study HfO2 as a dielectric for MOS capacitors over SiC substrate previously passivated. In order to a better understanding of the results, the same device will be made over Si substrate and compare with the SiC results.

Initially, double side polished SiC n-type (0001) and Si n-type (100) wafers were used. The samples were cleaned with RCA cleaning. The SiC sample was subjected to a passivation process with N2+O2 plasma at room temperature. Then, 35 nm of HfO2 was deposited by RF sputtering on substrates top (Si and SiC), follow by a lithography process to define the area of the capacitors. To finish the MOS devices, 300 nm of aluminum was deposited by thermal evaporation to provide electric contact (top and bottom).

From Fig. 1 (left image) we observe that the capacitor on Si presented Cmax, Cmin, and VFB in the order of 10-6 F, 10-7 F, and 0.02 V, respectively, which are better values than those reported in the literature for this substrate. Fig. 1 (right image) shows that the capacitor on SiC presented Cmax, Cmin, and VFB in the order of 10-6 F, 10-7 F, and 4.34 V, respectively. It is noted that the capacitance values remained in the same order of magnitude, with the greatest variation observed for the VFB value. The literature reports this same positive shift for VFB values for HfO2 oxides, sometimes even reaching 10V.

TF-ThP-7 Highly Improved Photocurrent Density and Power Conversion Efficiency of Perovskite Solar Cell by Inclined Plasma-Polymerized-Fluorocarbon Sputtering Process

Sang-Jin Lee, *M. Kim,* Korea Research Institute of Chemical Technology (KRICT), Republic of Korea

Plasma-polymerized-fluorocarbon (PPFC) thin films offer a promising solution to enhance the efficiency and durability of perovskite solar cells (PSCs). The PPFC thin film is manufactured using mid-range frequency (MF) sputtering. We enhanced the performance of MF sputtering by imparting conductivity to the target through the mixture of PTFE or PFA powder with carbon nanotube powder. When deposited on a transparent substrate, PPFC increases total transmittance and reduces reflectance due to its very low refractive index (~1.38). Additionally, the film exhibits hydrophobic surface, excellent mechanical flexibility, and high chemical stability. Application of the PPFC AR film to flexible PSCs increases PCE from 18.6% to 20.4% while maintaining excellent mechanical flexibility (bending radius: 4 mm) and high chemical stability. Moreover, an inclined sputtering process simultaneously realizes the AR effect of PPFC coating and F doping's impact on a TiO2 electron transport layer (ETL). Consequently, Jsc in rigid-type PSCs rises from 25.05 to 26.01 mA/cm2, and PCE from 24.17% to 25.30%. Thus, PPFC thin films enhance the long-term stability of PSCs in humid environments. Finally, these AR PPFC thin films can be manufactured using a large-area process, rendering them suitable for future use in highly efficient PSCs.

TF-ThP-8 The Effects of Ultraviolet Irradiation and Mechanical Stress on Polymer-Like Hydrogenated Amorphous Carbon Thin Films

T. Poché, R. Chowdhury, Y. Tesfamariam, ***Seonhee Jang,*** University of Louisiana at Lafayette

Polymer-like hydrogenated amorphous carbon (a-C:H) films have found use in many applications due to their desirable material properties. Compared to other a-C:H films, are characterized by having a high H content (40-50%) as well as a significant amount of C-H sp3 bond sites, and their properties are known to be highly tunable by various post-processing methods. One such method is ultraviolet (UV) irradiation, which can remove H from the film, assist in oxygen (O) absorption, and promote graphitization. The ability to selectively tune the properties of a film at specific locations is desirable for applications such as biomedical devices and warrants further research.For this study, a-C:H films were grown onto both rigid silicon (Si) (100) and flexible indium tin oxide/polyethylene naphthalate (ITO/PEN) substrates by the plasma-enhanced chemical vapor deposition of cyclohexane (CHex, C_6H_{12}) precursor. The a-C:H films were deposited at ambient temperature of 18-19 °C with varying plasma powers from 20 to 80 W. A 275 nm UV source was applied to the a-C:H films on rigid Si for various cure times of 1 and 4 hours, and various irradiances at 0.0022 and 0.0466 W/cm2. The most extreme of these curing conditions (4 hours at 0.0466 W/cm^2) was applied to the a-C:H films on flexible ITO/PEN, prior to 10,000 cycles of repeated mechanical bending. The thickness, refractive index, extinction coefficient, and optical bandgap of the a-C:H films were measured by spectroscopic ellipsometry. The surface wettability of the films was measured by contact angle goniometry, while the surface morphology and roughness were measured by atomic force microscopy (AFM). The chemical composition and relative H content of the films was measured by Fourier-transform infrared (FTIR) spectroscopy.UV irradiation caused ablation of the film surface, decreasing the film thickness. Simultaneously, H was preferentially removed from the film while O was incorporated from the atmosphere. The films remained optically transparent and topologically smooth after the UV irradiation procedure. The surface wettability of the films increased substantially, while the optical bandgap values decreased. The FTIR analysis supported that H removal and O incorporation occurred throughout the a-C:H films during UV irradiation. The mechanical bending procedures caused no significant changes to occur within the UV irradiated a-C:H films, indicating their potential for application in flexible electronic devices. In summary, UV irradiation plays an important role in tuning the composition, and thus the properties of polymer-like a-C:H films.

TF-ThP-9 Adoption of UV-Di for Fabricating Electrically Enhanced Amorphous In-Ga-Zn-O Thin-Film Transistors at Low Temperatures

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We investigated the electrical characteristics of sol-gel processed thin-film transistors (TFTs) and found that they are improved by the addition of UV-irradiated deionized water (DI water). The vulnerability of solution-processed metal-oxide semiconductors is significantly influenced by organic chemical-induced defects such as voids, holes, and organic residues. To address this issue, we introduced hydroxyl radicals (OH•), generated in DI water through an O3/UV process, into the In-Ga-Zn solution mixture to deposit IGZO active layers with fewer defects. The generation of hydroxyl radicals in DI water was confirmed by potassium iodide (KI)/ultraviolet-visible (UV-vis) spectroscopy analysis. The intensity of the absorbance peak at wavelengths of 290 nm and 350 nm increased with longer UV irradiation times on DI water. Additionally, we used the TG-DSC method to determine that organic materials in the IGZO solution mixture with ozonated water began to decompose at a lower temperature (121.6℃) than pristine IGZO solution mixture (144.5℃). Abrupt weight loss was also observed in the IGZO solution with ozonated water compared to pristine IGZO solution. The field-effect mobility and sub-threshold slope of the a-IGZO TFTs made with ozonated water were improved compared to the conventional process, increasing from 0.40 to 0.97 cm^2/V·s and decreasing from 0.34 to 0.29 V/dec, respectively. These results suggest that the addition of ozonated water to the sol-gel mixture is a simple method to achieve high-performance TFTs by reducing organic chemical-induced defects through low-temperature processing.

TF-ThP-10 Influence of Multi-Energy Ion Implantation of Cu and Ag Ions on the Electrical Properties of Graphene and Cyclic Olefin Copolymer Thin Films*, **Eva Štěpanovská**, J. Novák,* Nuclear Physics Institute of the Czech Academy of Sciences, Czechia*; P. Malinský,* Nuclear Physics Institute of the Czech Academy of Science, Czechia*; V. Mazánek,* University of Chemistry and Technology, Czechia*; M. Kormunda, L. Vrtoch,* J. E. Purkyne University, Czechia*; A. Macková,* Nuclear Physics Institute of the Czech Academy of Sciences, Czechia

Graphene (G) and cyclic olefin copolymer (COC) thin films with a thickness of 50 µm were subjected to multi-energy ion implantation of Cu^+ and Ag^+ ions. The ions were implanted with energies of (2.8, 2.0, 1.2) MeV and various fluences (10^{12}, 10^{13}, 10^{14}) ions/cm^2. Ion energy levels were chosen to create continuous layers within the organic materials, intersecting in a Gaussian distribution. Elemental changes were analyzed using Rutherford backscattering and elastic recoil detection analysis (RBS/ERDA), chemical bonds were monitored using X-ray photoelectron spectroscopy (XPS), infrared (IR) and Raman spectroscopy, and finally electrical properties were investigated using electrochemical impedance spectroscopy (EIS). With increasing ion fluence, the sheet resistance of the implanted layers decreases, indicating an increase in the material's electrical conductivity. This study provides a comprehensive insight into the changes in the microstructure and electrical properties of graphene and cyclic olefin copolymer thin films after ion implantation, which holds significant potential for applications in electronics and sensing.

TF-ThP-11 Study of Plasma-Polymerized Fluorocarbon Nano-Thin Films Deposited by Sputtering*, **Mac Kim**, J. Kim, S. Lee,* Korea Research Institute of Chemical Technology (KRICT), Republic of Korea

Recently, plasma-polymerized fluorocarbon (PPFC) thin films produced by a sputtering process have been investigated as a possible replacement for conventional polytetrafluoroethylene (PTFE) coatings. In this study, we fabricated a new type of polymer target composed of a mixture of PTFE and functional fillers, and it was deposited as PPFC thin films using a large-area roll-to-roll sputter. The crystal structure of PPFC thin films is amorphous and unlike PTFE, which is composed of only CF_2 bonds, PPFC thin films exhibit a chemical structure composed of CF, CF_2, CF_3, and C-CF_n bonds. Despite these structural differences, PPFC thin films exhibit similar properties to PTFE, including water repellency, electrical insulation, chemical resistance, and heat resistance. And unlike opaque PTFE, it is highly transparent in the visible light region due to its amorphous structure. PPFC thin films deposited with a CNT-PTFE composite targets with 1 wt% CNT content showed 93.27% transmittance at 550 nm wavelength and water contact angle above 100°. By controlling the type and amount of CNTs and additives in the composite target, the surface hardness of the PPFC thin film could be increased from 0.58 GPa to 6.9 GPa. From these results, we confirm that a high hardness PPFC thin film with high hydrophobicity, transparency and flexibility can be fabricated via mid-range frequency roll-to-roll sputtering. Therefore, multifunctional PPFC thin films are effective in improving the performance of flexible displays or solar cells and can be applied as surface protective coating thin films for electronic devices.

TF-ThP-12 Effect of Vanadium Substitution for Electron Correlations in CrN Thin Films*, **Shu Sawaya**, K. Bin Onn, T. Suzuki,* Nagaoka University of Technology, Japan

Chromium nitride (CrN), one of the strongly correlated electron systems, has attracted attention as a new material for magnetic-structural interactions due to its distinctive antiferromagnetic configurations. CrN exhibits a transition from high-temperature paramagnetic cubic to low-temperature antiferromagnetic orthorhombic crystals. Factors such as Cr/N ratio, polycrystalline/epitaxial, lattice distortion, thickness, substrate selection, and substrate orientation affecting the Néel temperature (T_N). Experimental and theoretical investigations which has been held over past years have provided a good understanding of the structural and magnetic properties of CrN. However, the electrical properties of CrN are still under debate, with the electronic structure being of particular interest. The electronic structure near the valence band of CrN is mainly formed by 3d electron bands, and the generation of the band gap is attributed to the electron correlation of the d electrons. Contradicted results have been reported regarding the electrical properties of CrN, ranging from Mott-Hubbard-type insulator, charge-transfer-type insulator, to pure metal.These contradictory reports indicate a lack of understanding the fundamental electronic structure of CrN.

In this study, substitutional solid solution of CrN and vanadium nitride (VN), denoted as $(Cr_{1-x},V_x)N$ were deposited by pulsed laser deposition to investigate the itinerant behavior of CrN in details. We focused on the electrical properties of $(Cr_{1-x},V_x)N$ thin films in which the electron correlation effect was reduced with x as a variable. In order to evaluate the true properties of $(Cr_{1-x},V_x)N$, MgO(001) were used as substrates, which can be prepared as near single crystals by epitaxial growth. The solid solution of VN substitution into CrN was controlled by changing the Cr/V surface area ratio of the target.

Figure 1(a) and (b) show the temperature dependence of the electrical resistivity of $(Cr_{1-x},V_x)N$ thin films deposited at substrate temperatures of 773 and 973 K respectively. At 773 K, CrN and VN exhibited metallic temperature dependence, whereas $(Cr_{1-x},V_x)N$, exhibited mostly insulating temperature dependence, contrary to expectations. Furthermore, the sample with $x = 0.09$ was exhibited no temperature dependence of resistivity. On the other hand, all samples prepared at 973 K exhibited metallic behavior. Systematic x-dependence was not observed in either result. The band gap caused by the difference in substrate temperature suggested that the electronic structure of $(Cr_{1-x},V_x)N$ may not solely given by electronic correlations, but may also involve Anderson localization due to the crystal state.

TF-ThP-13 Poly(P-Phenylenediamine) by oMLD for Amine Functionalization of Polydioxanone for Biomedical Applications*, **Nazifa Z. Khan**, N. Paranamana, X. Liu, M. Young,* University of Missouri-Columbia

Polydioxanone (PDO) is an aliphatic polyester with excellent biocompatibility, flexibility, and biodegradability, and has been widely used as a surgical suture. However, lack of functional groups in the backbone of PDO limits its applications to other biomedical aspects. Here, we study vapor-phase oxidative molecular layer deposition (oMLD) of an amine-containing polymer, poly(p-phenylenediamine) (PPDA), onto PDO substrates. Our goal with this is to use vapor-phase infiltration to form PPDA within PDO and provide stable surface amine groups for subsequent grafting of biomolecules. Recent work established oMLD growth of PPDA at 150 °C. Here, a lower deposition temperature is necessary for compatibility with PDO. We study oMLD growth of PDO at 90 °C, both onto flat silicon substrates and within the spin-coated PDO polymer. We employ *in situ* quartz crystal microbalance (QCM) studies during oMLD growth to benchmark the deposition of PPDA at these lower temperatures. We also report *ex situ* spectroscopy and chemical analysis on flats to understand the extent of amine incorporation into PDO and the stability of this PPDA polymer in physiologically relevant solution conditions. The incorporation of amine groups onto the PDO surface will facilitate the addition of bioactive components into PDO to control cell-material interactions, therefore expanding its application in regenerative medicine.

TF-ThP-14 Tuning the Crystallinity of TiO_2 Coatings Synthesized by an Atmospheric Pressure Dielectric Barrier Discharge*, **Nicolas Fosseur**,* Chemistry of Surfaces, Interfaces and Nanomaterials (ChemSIN), Faculty of Sciences & 4MAT, Engineering faculty, Université Libre de Bruxelles, Brussels, Belgium*; S. Godet,* 4MAT, Engineering faculty, Université Libre de Bruxelles, Brussels, Belgium*; F. Reniers,* Chemistry of Surfaces, Interfaces and Nanomaterials (ChemSIN), Faculty of Sciences, Université Libre de Bruxelles, Brussels, Belgium

Titanium dioxide (TiO_2) is a widespread semiconductor material present in numerous applications such as photovoltaic panels, various cosmetic products and batteries.Nowadays it is intensively studied for its depolluting action thanks to its photocatalytic properties. However, generating crystalline thin films using a cold plasma operating at atmospheric pressure is not trivial. This work focuses on the crystallization of anatase thin films, using a Plasma Enhanced Chemical Vapor Deposition method (PECVD). Different TiO_2 films are synthesized in an atmospheric pressure dielectric barrier discharge system, enhanced with an original heating device [1,2], and analyzed using scanning electron microscopy (SEM), X-ray diffraction (XRD), X-rays photoelectron spectroscopy (XPS) and Infrared reflection-absorption spectroscopy (IRRAS). The ultimate goal of this research is to better control the crystal size and the crystalline structure which are decisive parameters in the efficiency of the photocatalytic effect. To do so, different plasma depositions were done with a total flow of 10 slm (15% of argon flow going in the bubbler, 15 % of O_2 and 70 % of Argon carrier flow) and a deposition time of 20 minutes. By changing different parameters such as substrate temperature, power and frequency, a constant crystal size could be obtained and by increasing precursor temperature, crystal sizes ranges from 10 to 20 nm. At a larger scale, by tuning the frequency of the plasma generator, the coatings deposited exhibit different mean cauliflower-like size ranging from 570 to 975 nm, which influence the specific surface area. These preliminary results open a door on controlling more efficiently the crystal size, the crystal growth and the coating texture and density, which could help improving further photocatalytic applications.

Acknowledgments:
This project is funded by the FNRS PER Virusurf project and by the Fonds de la Recherche Scientifique – FNRS under the *Synthesis of crystalline N-TiO$_2$ via NTP* project.

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Keywords: anatase, atmospheric pressure plasma, crystal size, bubbler temperature, photocatalytic application.

TF-ThP-15 Simultaneous Nanopatterning of SiO$_2$ and Ru via Area-Selective Atomic Layer Deposition

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Area-selective atomic layer deposition (AS-ALD) has emerged as a promising technique for precisely controlling thin film deposition on desired areas. When combined with other fabrication methods, AS-ALD can address existing challenges in nanopatterning fabrication. In this study, ruthenium AS-ALD was integrated with an area-selective etching (ASE) process to achieve self-aligned nanopatterns. Tricarbonyl (η4-2-methylene-1,3-propanediyl)Ruthenium(II) (TRuST) and O_2 were used as as novel Ruthenium precursor and reactant, respectively, for Ru AS-ALD. The bis(N,N-dimethylamino)dimethylsilane (DMADMS) served dual roles: as a precursor in SiO_2 ALD and as an inhibitor in the Ru AS-ALD process. During Ru AS-ALD, DMADMS selectively adsorbed on SiO_2 surfaces, effectively blocking Ru film growth, but not on the Ru substrate surface. Subsequently, O_3 was introduced as a counter reactant for SiO_2 ALD, reacting with DMADMS-adsorbed SiO_2 surfaces to grow ALD SiO_2 and simultaneously etching Ru from the Ru substrate surface. By controlling the selectivity of Ru using DMADMS and the O_3 exposure time, desired thicknesses of Ru and SiO_2 films were achieved, enabling controlled Ru/SiO_2 nanopatterning in a single combined AS-ALD and ASE process. The adsorption of the DMADMS inhibitor, the selectivity and etching of Ru, and the growth of SiO_2 films were investigated using several analytical techniques including X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), scanning electron microscopy (SEM), in-situ spectroscopic ellipsometry (SE), and in-situ quadrupole mass spectrometry (QMS).

TF-ThP-16 Deposition of Novel (Cr,Yb)(N,O) Thin Films and Its Mechanical Properties

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The substitution of ternary and even quaternary elements into chromium nitride (CrN) based thin films has been documented to significantly enhance their mechanical properties. This is particularly relevant in response to the growing demand for coatings that provide high hardness, wear resistance, and oxidation resistance. Specifically, ternary systems such as Cr-Al-N and Cr-Ti-N, based on binary Cr-N thin films, have attracted substantial interest within the academic and industrial research communities. These systems are being intensely studied for their potential to meet the stringent requirements of advanced coating applications. Recent studies have particularly focused on the incorporation of ytterbium (Yb) as a ternary element in Cr-Yb-N thin films. The findings have shown that the addition of Yb markedly improves the hardness of the films compared to pure CrN thin films. This enhancement is attributed to the unique properties of ytterbium, which can influence the microstructure and stress distribution within the film. Moreover, ytterbium(II) oxide (YbO), which crystallizes in the same rock-salt structure as CrN, presents a promising avenue for substitution solutions. The structural compatibility of YbO with CrN suggests that it could be integrated into CrN thin films without significant lattice mismatch, potentially leading to improved film performance.

In this study, homogeneous chromium nitride (CrN) thin films with ytterbium (Yb) incorporated as a ternary element and oxygen (O) as quaternary element denoted as (Cr,Yb)(N,O) were deposited using the pulsed laser deposition (PLD) technique. The deposition process was conducted on silicon (Si (001)) and glassy carbon (G.C.) substrates, ensuring ultrahigh vacuum conditions with pressures maintained below $<1\times10^{-6}$ Pa. The substrate temperature (T_{Sub})was consistently held at 773 K to facilitate optimal film growth and adhesion. Cr and Yb metals were used as targets, with the surface ratio of Yb controlled at 10%. Oxygen gas through variable leak valve and nitrogen radicals was introduced into the deposition chamber, creating a controlled atmosphere. The deposited thin films were characterized using X-ray diffraction (XRD), Rutherford backscattering spectrometry (RBS), and nanoindenter. These provided insights into crystallographic structure, elemental composition, and mechanical properties, respectively. XRD analysis indicated peak shifts to lower angles with oxygen content below 10% and to higher angles above 10%, suggesting changes in lattice parameters. Nanoindentation results showed maximum hardness for oxygen content below 10%.

TF-ThP-17 Direct Growth of Molybdenum Disulfide from Metal Contacts via Atomic Layer Deposition

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As current silicon-based transistor devices begin to approach the fundamental material scaling limits of silicon, new designs and material integration methods are required to meet the ever-increasing demand for greater computing power and memory storage densities. Molybdenum disulfide (MoS_2) is one material in the two-dimensional materials class which is a potential replacement for silicon within next generation microelectronic devices to enable further device scaling due to its high electron mobility, even when in monolayer form. High quality MoS_2 is required for integration into microelectronic devices as even small concentrations of defects can significantly impact the electrical properties of the monolayer film. Synthesis of monolayer MoS_2 which is of sufficient quality for integration into microelectronic devices while maintaining processing temperatures that are within the allowable thermal budget of back end of line processing has proven difficult. In this work we demonstrate a method of growing crystalline MoS_2 directly from contact metals via atomic layer deposition (ALD) using molybdenum hexafluoride and hydrogen sulfide as the reactants. Several different contact metals including tungsten, molybdenum, nickel, and platinum were used for blanket studies to determine the ability to deposit crystalline MoS_2 at low temperatures. Raman spectroscopy was used to examine the crystallinity of the deposited films and x-ray photoelectron spectroscopy was utilized to determine the chemical composition of the deposited films. To obtain high quality MoS_2 test structures, contact metals were patterned to template direct ALD of MoS_2. Following MoS_2 deposition the samples were again characterized using Raman spectroscopy and atomic force microscopy to determine the crystallinity and morphology of the resulting MoS_2 film.

TF-ThP-18 Unlocking the Potential of Porphyrin-Based Covalent Organic Frameworks Through Vapor-Phase Synthesis of Thin Films: Process Optimization

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Porphyrin-based covalent organic frameworks (COFs) hold immense promise in various applications such as catalysis, solar cells, biomedicine, and environmental science due to their intrinsic porosity and programmable function. However, the insolubility of most two and three-dimensional covalently bonded materials poses a challenge for their integration as electroactive components. To address this limitation, thin-film growth techniques have emerged as a pivotal approach, particularly in the case of 5,10,15,20 tetra-4-aminophenyl porphyrin (TAPP) based COFs (POR-COFs). This work explores the vapor-phase synthesis route for the growth of POR-COF thin films, facilitating their integration into complex geometries for diverse applications. The synthesis process involves sequential delivery of TAPP precursor molecules and oxidants into the reaction zone, with excess materials and byproducts removed during purge cycles. Temperature and pressure are identified as key parameters governing the deposition process, alongside the exposure time of the substrate to impinged molecules. Through meticulous examination utilizing quartz crystal microbalance (QCM), atomic force microscopy, ellipsometry, and scanning electron microscopy, the effects of temperature and pressure on thin-film thickness and deposition rate are elucidated. The correlation between process parameters and surface coverage is investigated to enhance film quality and gain deeper insights into the growth process of POR-COFs thin films. This research not only contributes to the understanding and optimization of thin-film growth techniques but also paves the way for the utilization of COFs in various advanced applications.

TF-ThP-19 The Stability of Lif-Capped Fluorinated Aluminum Films When Irradiated with Electrons

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Aluminum thin films are an ideal broadband reflectors for application including space observatories. However, oxide forms on freshly-deposited Al when it is exposed to oxygen or water vapor. This oxide layer absorbs a large portion of far ultraviolet (FUV) wavelengths. In order to prevent oxidation a barrier layer layer is deposited on top of Al mirrors. To preserve high FUV reflectance it is usually a low Z metal fluoride, such as MgF_2, AlF_3 or LiF. Of the commonly used metal fluorides, LiF has the best FUV transparency. However, it is susceptible to radiation damage. Many studies have shown that the electron beam in an electron microscope (SEM or TEM) can damage halide salts such as sodium chlorides and bromides. One such process termed radiolysis. Alkali halide salts are known to be most sensitive. The halide anion disappears as does the cation. Since mirrors on space telescopes will also be exposed to the solar wind and coronal mass ejection (CME) understanding the degradation mechanism and kinetics was deemed a high priority. We have studied the radiolysis of fluoride films important to FUV optics, mainly LiF films. The first damage is a roughening of the surface and a decrease of the fluorine peak in energy dispersive x-ray analysis (EDX). Note that, lithium (Z = 3) cannot be detected by x-ray florescent techniques since its electrons are not sufficiently bound. In some cases, LiF is fully removed from the scanned region after beam exposure.

TF-ThP-20 Achieving a Low-Voltage Operation Indium Gallium Zinc Oxide Thin Film Transistor Through Optimized Crystallinity ZrO_2 Gate Insulator

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The indium gallium zinc oxide (IGZO) has been widely investigated as the active layer for the display backplane thin-film-transistor (TFT). In ultra-high-resolution displays, reducing transistor size per pixel results in submicron-scale channel lengths.[1] Consequently, the short-channel effects become a concern as TFT channel lengths decrease to the submicron scale. Novel architectures such as 3-dimensional vertical or FinFET structures would be developed. The fast-operation speed and low-voltage operation of TFTs are made possible by using the gate insulator (GI) with a high-dielectric-constant (k) value. Among many high-k materials, ZrO_2 has a high-k value (28) and a suitable band gap (5.8 eV).[2] Atomic layer deposition (ALD) has the advantages of conformal depositions, thickness/composition controllability of thin films, and thin film quality due to its self-limiting growth behavior.

High-k materials exhibit higher dielectric constants compared to amorphous-phase SiO_2 due to their crystallinity.[3] However, high-k materials used as GI result in TFT performance degradation due to increased surface roughness caused by crystallinity, increasing surface scattering, and coulomb scattering. In the previous study, our research group controlled the crystallinity of ZrO_2 by varying the deposition temperature and optimized ZrO_2 ALD processes in $Mo/ZrO_2/IGZO$ metal-insulator-semiconductor structures.[4] In this study, we investigated ALD-derived IGZO TFTs using an optimized ZrO_2 ALD process.

The ZrO_2 film was deposited by the thermal ALD process using Cyclopentadienyl Tris(dimethylamino)Zirconium (CpZr), and ozone (O_3). The IGZO film was deposited by thermal ALD process using STIn-7-7, trimethyl gallium (TMGa), and diethyl zinc (DEZ) precursors. O_3 was used as a reactant. The deposited film characteristics were evaluated using glancing incidence X-ray diffraction, atomic force microscope, and X-ray fluorescence spectroscopy. The ALD-derived IGZO TFTs with a bottom gate staggered structure were fabricated. The electrical properties of the TFTs were measured using a 4156C precision semiconductor parameter analyzer.

AcknowledgmentsThis work was supported by the BK21 Plus program.The authors would thank SK Trichem for their support and permission to publish this collaborative work.

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TF-ThP-21 Suppressing the Interfacial Layer Formation between Metal Electrode and Insulator by Employing Molybdenum Dioxide Electrode

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Semiconductor devices, especially dynamic random-access memory (DRAM), are achieving high-density integration and remarkable technological development continuously. At the forefront of advancement in the DRAM device was the introduction of high dielectric constant (high-*k*) materials, which significantly increased its memory capacity. Especially, since the introduction of ZrO_2 as a high-*k* material, TiN electrode has been widely used as the electrode for DRAM capacitor application, owing to its crystallinity coherent with ZrO_2 [1][2]. However, due to the oxygen scavenging effect of TiN, low-*k* TiO_xN_y interfacial layer is formed between the TiN electrode and oxide. The oxygen scavenging effect generates oxygen vacancies in ZrO_2, leading to increase in leakage current. This is because the leakage current mechanism of ZrO_2 is attributed to the presence of oxygen vacancy [3]. Additionally, meeting the requirement of low leakage current for practical DRAM applications in aggressively scaled devices becomes challenging since the TiN electrode has a low work function (~4.3 eV), which reduces conduction band offset [3]. Therefore, in this work, we investigated suppressing the oxygen scavenging effect of TiN electrode using molybdenum dioxide (MoO_2) electrodes, aiming to reduce the concentration of oxygen vacancy in the ZrO_2 and leakage current.

MoO_2 is proposed as a novel oxide electrode for DRAM capacitor, owing to its high work function and excellent chemical stability [2]. To mitigate the oxygen scavenging effect of TiN and reduce leakage current, we compared TiN and MoO_2 electrodes in ZrO_2-based metal-insulator-metal (MIM) capacitors and analyzed the oxygen vacancy defects and electrical properties. Oxygen vacancy defects in ZrO_2 were investigated through AC nonlinearity in the C/C_0–V_{ac} (where C_0represents capacitance at zero V_{ac}) [4] and XPS analysis. This revealed a reduction of defect sites induced by oxygen vacancy within ZrO_2 when introducing MoO_2 electrodes. Moreover, it should be noted that the decrease in defect sites induces a reduction in leakage current.

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TF-ThP-22 Controlling the Electrical Properties of ZrO_2 Dielectric Films by Employing Sc_2O_3

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Dynamic random-access memory (DRAM) is extensively employed in various industrial sectors as a prominent semiconductor component. Among them, there is a trend toward scaling down DRAM capacitors with MIM (metal-insulator-metal) structure to achieve high capacitance and low leakage current ($<10^{-7}A/cm^2$) at operating voltage. However, scaling down also resulted in decreased the thickness, thereby reducing the area of capacitor and subsequently decreasing the amount of charge that can be stored. Consequently, high dielectric constant materials such as ZrO_2 and HfO_2 are employed as insulators to mitigate this issue. Hence, the conventional DRAM MIM capacitor commonly employs TiN for both top, bottom electrodes, while utilizing ZrO_2 as the insulator. ZrO_2 exists in three phases: monoclinic, tetragonal, and cubic. Among them, ZrO_2commonly used in DRAM is manufactured via an atomic layer deposition process and exhibits a high dielectric constant (~40) in its tetragonal phase. However, there are several problems. Crystallized ZrO_2 monolayers exhibit high leakage currents due to carrier conduction paths formed by grain boundaries.[1]

Therefore, in this presentation, we demonstrate the results of employing Sc_2O_3 to improve the electrical properties of ZrO_2 dielectric film. Sc_2O_3has a high dielectric constant ($\varepsilon = 13$) and a large band gap (Eg=~6 eV). [2]We expect that the wide band gap of Sc_2O_3 will serve as a barrier in the carrier conduction path. Using these properties, we conducted two experiments via the ALD process. First, we examined the effectiveness of Sc doping into ZrO_2. Second, we precisely inserted a Sc_2O_3 monolayer between ZrO_2 insulating layers to see how it affects the performance of ZrO_2 based MIM capacitor. Moreover, we performed crystal phase analysis and evaluation of electrical properties to investigate the effect of Sc incorporation.

Acknowledgments: This work was supported by the BK21 Plus program. The authors would like to thank SK Trichem for their support and permission to publish this collaborative work.

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TF-ThP-23 Influence of Different Oxygen Sources on the Optical Properties of HfO_2 Films Grown by Atomic Layer Deposition*, B. Xherahi,* Community College of Philadelphia, Philadelphia, PA 19130,USA*; S. Azadi, D. Barth,* ***Lucas Barreto,*** Singh Center for Nanotechnology, University of Pennsylvania, Philadelphia, PA 19104, USA

Hafnia (HfO_2) stands as a promising option for substituting SiO_2 on transistors due to its high dielectric constant. Furthermore, its high band gap provides transparency over a wide spectral range, which makes it applicable for optical coatings. Hafnia also presents a high index of refraction and excellent thermodynamic stability, and its orthorhombic phase exhibits a ferroelectric response. Among the different HfO_2 fabrication strategies, atomic layer deposition (ALD) is a reliable method for obtaining high-quality conformal hafnia films. Adjusting the process parameters and using different precursors can lead to variations in the resulting film properties. This work evaluates how the deposition temperature and the ALD oxygen source change the hafnia films deposited on Si(100). We use tetrakis(dimethylamido)hafnium (TDMAH) as the metal precursor, and we compare the properties of the films for two distinct oxygen precursors: H_2O and O_3. We measure the deposition rate and index of refraction using ellipsometry and correlate the results with the ALD oxygen source and deposition temperature. The results of this work provide insights for adjusting ALD deposition conditions to tune hafnia properties.

TF-ThP-24 ZnSe as Window Layer for n-CdTe Solar Cells*,* ***Wei Wang****, V. Palekis, M. Zahangir, S. Elahi, C. Ferekides,* USF Tampa

ZnSe as Window Layer for n-CdTe Solar Cells

To overcome the V_{OC} bottleneck for traditional p-CdTe solar cells, polycrystalline n-type CdTe thin films were used as the absorber layer. Polycrystalline n-type CdTe films were deposited by the elemental vapor transport (EVT) process. The EVT process can be used to deposit CdTe films under Cd- or Te-rich conditions to facilitate extrinsic doping. Indium as n-type dopant is used to increase the CdTe conductivity. A proper p-type partner is critical to form a p-n junction with the n-CdTe absorber. A ZnSe layer was used as the p-type partner of n-CdTe solar cells. The device structure includes Glass/ITO/CdS/n-CdTe/p-ZnSe:Cu/ITO. The ZnSe layer was deposited by RF sputtering followed by the deposition of a thin Cu layer. This work investigated the effect of ZnSe as a window layer for n-CdTe solar cell, specifically: (1) the substrate temperature during ZnSe deposition; (2) Cu thickness. In addition, the effect of ZnSe as an interfacial layer for n-CdTe/p-ZnTe solar cell was studied as well. The device structures were characterized by current-voltage (J-V), spectral response (SR), and capacitance-voltage (C-V) measurements.

ZnSe thin film as an interfacial layer for n-CdTe/p-ZnTe devices causes a “kink” in the J-V curve, which is due to the large valence band offset at CdTe/ZnSe. Two substrate temperatures of depositing ZnSe thin films were studied (i.e., 250℃ and 350℃), when it was used as p-type partner of n-CdTe solar cell. The devices where the ZnSe films was deposited at 350℃ showed higher carrier collection from the SR data. Cu layers with thicknesses of 5Å and 15Å were deposited after ZnSe. Devices with larger amount of Cu exhibit lower carrier collection resulting in lower device performance.

TF-ThP-25 Understanding the Surface Chemistry of Tin Halide Perovskite Thin Films*,* ***Mirko Prato****, A. Treglia, I. Poli, A. Petrozza,* Istituto Italiano di Tecnologia, Italy

Tin halide perovskites (THP - general formula: $ASnX_3$, A: Cs^+, MA = $CH_3NH_3^+$, FA = $NH_2CHNH_2^+$; X: I^-, Br^-, Cl^-) have emerged as promising alternatives to toxic lead perovskites in next-generation photovoltaics.

One of the overwhelming obstacles to improving device performance is the high carrier concentration originating from Sn vacancies, resulting in self p-doping and affecting the optoelectronic properties of the material. Simultaneously, the facile oxidation of Sn^{2+} to Sn^{4+} further contributes to increasing the p-doping in the bulk and non-radiative recombination centers on the surface.

One effective approach to reduce the presence of oxidized species within the material is to add reducing agents directly within the precursor solution in the form of additives. The most used and effective is SnF_2, which promotes a slower crystallization and improved film quality and effectively limits the self-p doping effect.

While the oxidation of Sn perovskites and its suppression are frequently discussed in the literature, the mechanisms involved and the role of SnF_2 in protecting the film against oxidation are still uncertain and under debate. We therefore investigated the role of tin fluoride in defining the complex surface chemistry of tin halide perovskite thin films, prepared via solution processing. We show that oxygen is found on the surface of tin perovskite thin films even if never exposed to ambient air; however, the use of SnF_2 in the precursors solution strongly affects the chemical nature of the found species. Indeed, oxygen primarily binds to tin in the form of SnO_2 only when SnF_2 is added to the precursor solution, while it is mainly due to adventitious species when SnF_2 is not used. We therefore highlight that the presence of a predominant single chemical state in the XPS Sn core level does not necessarily correspond only to Sn^{2+} species in the perovskite form but could also indicate the formation of superficial SnO_2. Finally, we show that SnF_2 does not help in avoiding nor slowing down the degradation of the perovskite film when exposed to ambient air and that oxidation occurs on the whole-grain surface. These results provide insightful guidance toward understanding oxidation in tin halide perovskites and elucidating its detrimental effect onmaterial’s properties.

2D Materials
Room 122 - Session 2D+EM+MN+TF-FrM
2D NEMS and Strain Engineering

Moderators: Susan Fullerton, University of Pittsburgh, **Peter Sutter**, University of Nebraska

8:15am **2D+EM+MN+TF-FrM-1 Engineering the Structure and Properties of 2D Materials by Defects, Strain and Intercalation***, **Arkady Krasheninnikov**,* Helmholtz Zentrum Dresden-Rossendorf, Germany**INVITED**

As 2D materials have a high surface-to-volume ration, nearly all of them contain defects and impurities, which may have appeared due to the effects of the environment or exfoliation, or in case of synthetic materials, during the growth. The defects can govern the electronic and optical properties of 2D systems. Moreover, defects can intentionally be introduced using beams of energetic particles – ions and electrons. Formation of defects may also give rise to phase transformations in these materials and/or tune their properties. Mechanical strain and intercalation by, e.g., alkali metal atoms, can further be used to tailor the materials characteristics. All of these calls upon the studies on defects and their role upon intercalation, response of materials to strain and irradiation. In my talk, I will present the results of our recent theoretical studies of point and line defects in 2D materials [1-4] obtained in close collaboration with several experimental groups. I will further discuss how strain can affect the characteristics of defective 2D materials [5] and how new 2D phases of materials can be created upon atom intercalation between graphene sheets and address the role of defects in this process [6].

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8:45am **2D+EM+MN+TF-FrM-3 Band Gap Opening in AB-Stacked Bilayer Silicon***, **Kumar Vishal**, H. Huang, Y. Zhuang,* Wright State University

Despite their potential as of being the excellent candidates for advancing CMOS technology to its physical limits, the presence of an opened energy bandgap in either single- or bilayer- silicene poses a significant challenge, hindering its applications in the main stream semiconductor industry. Previous attempts, including applying external electric field, surface decoration, nanopatterning, and applying uniaxial strain along designate directions, have proven insufficient in meeting the stringent demands of CMOS technology concerning operational reliability, processing environment sensitivity, product yield, and achievable processing standards. Recently a number of research reported that applying of the biaxial in-plane strain leads to energy bandgap opening in AA-stacked bilayer silicene, however the maximum energy bandgap opening is limited to 16 meV.

In this work, we present a theoretical study of the opening of energy bandgap in AB-stacked bilayer silicene. Employing the Density Functional Theory (DFT), our investigations have taken into account of the effects of both ferromagnetism and antiferromagnetism, alongside external biaxial in-plane strain/stress and vertical biasing effects. Within a strain range spanning from -5.17% to 10.35%, we observed a strain-tunable energy bandgap opening with a maximum of 380 meV at a strain level of 7.76%. Notably, beyond this strain range, the energy bandgap remains closed. In addition, under compressive strain, the energy band diagram presents spin-generated features, with discernible energy band splitting. On the contrary, tensile strain leads to a break of the spin generation, except at specific high symmetry points such as Γ, K and M. We further observe a degeneration of the energy band diagram at these high symmetry points upon the application of gate voltage along the vertical direction. The coupling of the ferromagnetism and antiferromagnetism between the two silicene layers results in a transition from metallic material to semiconductor. The potential of the opened bandgap makes the AA-stacked bilayer silicene a very promising candidate material to be applied in the CMOS technology, while the strain-induced tunable bandgap opening offers immediate potential for applications in the infrared (IR) spectrum. In addition, the spin-induced band diagram degeneration may holds promise for integrated spintronics applications.

9:00am **2D+EM+MN+TF-FrM-4 Laser-Induced Strain Tuning in Monolayer Graphene Nanomechanical Resonators***, **Muhammad Ashar Naveed**, S. Pandit, Y. Wang,* University of Nebraska - Lincoln

Graphene, as the paradigm-shifting two-dimensional (2D) material, has demonstrated great potential in micro-/nano-electromechanical systems (MEMS/NEMS) due to its extraordinary mechanical properties, ultimate device thicknesses, and unparalleled flexibility in integration. On the other hand, the atomic thickness and the transfer process employed in device fabrication pose challenges to achieving uniform strain over the entire device. In this work, we utilize Raman spectroscopy and investigate the strain distribution in drumhead resonators based on the mechanically exfoliated graphene monolayers suspended over patterned oxidized silicon (SiO_2/Si) substrates. Moreover, the effects of laser-induced heating and consequential strain tuning have been systematically explored by combining Raman spectroscopy and mechanical resonance measurements. This study sheds light on the strain engineering of monolayer graphene nanomechanical resonators, and the methodology developed is readily applied to other 2D materials and heterostructures.

9:15am **2D+EM+MN+TF-FrM-5 Developing 2D Snse for Piezoelectric Applications***, J. Chin, M. Frye, B. Gardner,* Georgia Institute of Technology*; D. Liu,* Penn State University*; M. Hilse,* Pennsylvania State University*; I. Graham,* Georgia Institute of Technology*; J. Shallenberger, K. Wang, M. Wang, Y. Shin, N. Nayir, A. can Duin, S. Law,* Pennsylvania State University*; **Lauren Garten**,* Georgia Institute of Technology

Unique functionalities can arise when 2D materials are scaled down near the monolayer limit. Tin selenide (SnSe) is one such 2D material which is centrosymmetric in bulk but becomes non-centrosymmetric when reduced to the monolayer limit, enabling piezoelectricity, and potentially, ferroelectricity. Developing 2D piezoelectric and ferroelectric materials is critical for the scaling of efficient sensors and electronics, such as ferroelectric field effect transistors. However, unlike other 2D materials, the strong interlayer bonding makes exfoliating a monolayer of SnSe challenging. Therefore, direct film growth is necessary to control the layer thickness and promote lateral growth large enough for device testing. This talk will focus on the development of processing routes to control the morphology and layering of SnSe thin films grown by molecular beam epitaxy (MBE) for piezoelectric devices. The bulk *Pnma* phase of SnSe is stabilized over a broad range of Sn:Se flux ratios from 250 – 300 °C on (100) MgO and (0001) Al_2O_3 substrates. Changing the flux ratio did not affect the SnSe film stoichiometry; increasing the flux ratio only changes the predominant crystallographic orientation. ReaxFF molecular dynamics (MD) show that the limited stoichiometric change is due to the formation of Se clusters that weakly interact with the surface of the SnSe particles. Changing the temperature, flux ratios, and flux timing had a significant impact on the morphology and orientation of the SnSe thin films. Machine learning was used to infer the critical processing parameters that are needed for creating an oriented, wafer-scale thin film. Overall, this study identifies the conditions for the growth of monolayer SnSe thin films necessary for the development of 2D piezoelectric devices.

9:30am **2D+EM+MN+TF-FrM-6 Two-Dimensional (2D) $FePS_3$ Nanoelectromechanical Resonators with Local-Gate Electrostatic Tuning***, **Yunong Wang**, S. Yousuf, X. Zhang, P. Feng,* University of Florida

Nanoelectromechanical systems (NEMS) based on 2D magnetic materials are promising candidates for exploring ultrasensitive detection and magnetostrictive phenomena due to their high mechanical stiffness, high strength, and low mass. The resonance frequency of the suspended membrane resonator can be probed optically and manipulated mechanically via electrostatically induced strain. This makes electrostatic frequency tuning of the 2D magnetic NEMS resonator a promising way for exploring the novel magneto-mechanical coupling mechanism. Towards building magneto-mechanical coupling NEMS devices, we fabricated circular drumhead $FePS_3$ NEMS resonators with different cavity-diameter sizes (3um to 7um). In this work, we report on experimental demonstrations of high-performance antiferromagnet $FePS_3$ drumhead resonators with the highest frequency tuning range up to 31.62%. We further perform analytical modeling to gain insight and quantitative understanding of the frequency scaling law for $FePS_3$ drumhead resonators. Combining our experimental results and analytical modeling of the resonances, we resolved the elastic behavior of $FePS_3$, including the transition from ‘membrane-like’ regime to ‘plate-like’ regime, with built-in tension (γ) ranging from 0.1 to 2N/m. This study not only offers methods for characterizing the mechanical properties of ultrathin membranes of magnetic 2D materials but also provides important guidelines for designing high-performance magnetic NEMS resonator devices and opens possibilities for building drumhead resonator devices to exploit strain- and dynamics-engineered applications based on ultrathin magnetic 2D crystals.

9:45am **2D+EM+MN+TF-FrM-7 Tunable Phononic Frequency Combs in Atomically Thin Resonators***, **S M Enamul Hoque Yousuf**, T. Kaisar,* University of Florida*; J. Lee,* University of Central Florida*; S. Shaw,* Florida Institute of Technology*; P. Feng,* University of Florida

Phononic frequency comb (PnFC), the analogue of optical frequency comb in the radio frequency (RF) regime, has attracted significant research interest due to its potential applications in sensing and computing. In this abstract, we report on PnFCs generation via an atomically thin molybdenum disulfide (MoS_2) nanoelectromechanical resonator. We first measure the nonlinear mode coupling coefficient (λ) due to 1:1 internal resonance from the first-principles approach. To describe the energy exchange between the coupled modes, we employ two resonator equations with a single dispersive coupling term to model the response. The coupled mode equations are solved using the method of averaging to derive a closed form expression for the nonlinear mode coupling coefficient.To calibrate the vibration amplitude of both modes in the displacement domain, we measure the undriven thermomechanical noise.The nonlinear shift of the resonance frequency of mode 1 (f_1) that results from the dispersive coupling to mode 2 is measured as we drive mode 2 near its natural frequency (f_2). We estimate the mode coupling coefficient using our derived model.Additionally, we investigate the impact of Duffing nonlinearity on the energy cycling of the modes.

We utilize the 1:1 internal resonance to couple energy between two modes. The resonator response can be tuned from stable periodic response to quasi-periodic response by controlling external perturbation signals, such as DC gate voltage, RF drive voltage and frequency. The resonator exhibits three unique comb regions with well-defined comb structure. We observe that the periodic and quasiperiodic branches exist for a particular drive voltage and frequency, based on distinct initial conditions. Our demonstration leads the way to achieving tunable PnFCs in nanoscale devices to study nonlinear modal interactions and build ultrasensitive sensors and computing devices.

10:00am **2D+EM+MN+TF-FrM-8 Longitudinal Sound Speed Determination in 2D Semiconducting Crystal of GaS by Broadband Time-Domain Brillouin Scattering***, **Watheq Al-Basheer,*** King Fahd University of Petroleum & Minerals, Saudi Arabia*; C. Viernes, R. Zheng, S. Netzke, K. Pichugin, G. Sciaini,* University of Waterloo, Canada

Due to their unique structure and exceptional physicochemical characteristics, 2D semiconducting materials like GaS have recently attracted significant interest, making them viable options for numerous photonic industries and applications. In this study, time-domain broadband Brillouin scattering measurements were performed on a single, flake-like gallium sulfide (GaS) crystal to determine the out-of-plane longitudinal sound speed, evaluated at (3140 ± 20) m/s. As a member of the group-III monochalcogenide semiconductors, GaS has recently attracted significant attention owing to its remarkable semiconducting properties.Moreover, its high absorption coefficient and efficient carrier mobility have made it a perfect candidate in many photonic and optoelectronic applications and industries, such as fast UV photodetectors,hydrogen evolution catalysis, field-effect transistors,energy storage, gas sensing, and nonlinear optics. The reported results demonstrate the effectiveness of this non-destructive, all-optical technique for investigating the elastic properties of fragile 2D layered materials and provide the value of the out-of-plane compressive elastic constant,

Keywords

Time-domain Brillouin scattering, coherent acoustic phonons, broadband transient spectroscopy,

elastic constant, sound speed, 2D semiconductors, GaS, layered materials.

Plasma Science and Technology
Room 124 - Session PS+TF-FrM

Plasma Processes for Coatings and Thin Films

Moderators: François Reniers, Université Libre de Bruxelles, Belgium, **Scott Walton**, Naval Research Laboratory

8:15am **PS+TF-FrM-1 Interaction of Polycrystalline Aluminum Oxide and Sapphire Surfaces with Halogen-Containing Plasmas and Gases***, **Takuya Ishihara**, H. Tochigi,* Azbil corporation, Japan*; H. Kang,* Osaka University, Japan, Republic of Korea*; T. Ito, K. Karahashi, S. Hamaguchi,* Osaka University, Japan

In semiconductor manufacturing processes such as dry etching or chemical vapor deposition, capacitance manometers are widely used as essential vacuum pressure sensors to monitor and control the pressures of process gases. These gauges must be corrosion-resistant against process gases such as halides and their radicals generated by the plasmas. The diaphragm material of the manometer is especially important because, if its surface is altered by such corrosive gases, the sensor would send imprecise output signals possibly with the zero-point drift or pressure sensitivity shift. The errors are caused by the changes in mechanical properties of the diaphragm arising from the formation of the modified surface layer. For this reason, Ni-based alloys or polycrystalline ceramics of aluminum oxide (Al_2O_3) are typically used as the diaphragm material of capacitance manometers. More recent capacitance manometers employ sapphire (single crystal α-Al_2O_3) as their diaphragm material, which is of specific interest in this study[1]. Recent studies on the interactions of polycrystalline Al_2O_3 with fluorine-containing plasmas indicated the formation of aluminum fluoride layers on Al_2O_3 exposed to such plasmas [2-6]. In this study, ion beam experiments were performed, aiming to understand the surface modification mechanisms of Ni-based alloys and polycrystalline Al_2O_3 film by fluorine-containing plasmas. With the irradiation of energetic F^+ and Cl^+ ions, it was found that the typical etching rates of Al_2O_3 are about one-half of those of Ni-based alloys. It was also found that the fluorinated layers of Al_2O_3 were thinner than those of Ni-based alloys. In addition, surfaces of sapphire samples were exposed to xenon difluoride (XeF_2) gases for 3 and 6 months. The sapphire surface was fluorinated over the first 3 months, but the depth of the fluorinated layer did not increase much after 6 months. It indicates that a diaphragm made of pre-fluorinated sapphire may be able to prevent the signal shift of the manometer used under highly corrosive conditions in semiconductor manufacturing.

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8:30am **PS+TF-FrM-2 Development of Corrosion-Resistant, Low-ICR aC and TiN Coatings Using HIPIMS for Bipolar Plate Manufacturing for Hydrogen Fuel Cells***, **Nicholas Connolly**,* University of Illinois at Urbana-Champaign*; Z. Jeckell,* University of Illinois Urbana-Champaign*; R. Paul, M. Hysick,* Starfire Industries*; M. Hossain, B. Jurczyk, D. Ruzic,* University of Illinois Urbana-Champaign

Bipolar plates (BPPs) are a critical component in proton exchange membrane fuel cells (PEMFCs) that provide conducting paths for electrons between cells, distribute and provide a barrier for reactant gases, remove waste heat, and provide stack structural integrity. Stainless steel, specifically 316L, BPPs possess high electrical and thermal conductivity, good gas impermeability, and superior mechanical properties and formability. However, stainless steel has relatively low corrosion resistance and high contact resistance in the hydrogen fuel cell stack. Additionally, to meet the Department of Energy (DOE) cost/kW target for hydrogen fuel cells, recycling of the BPPs is practically a necessity.

In order to address these challenges, we will present work on two complementary studies. The first study is deposition of conformal amorphous carbon (aC) and titanium nitride (TiN) thin films using HIPIMPS with positive cathode reversal. The interfacial contact resistance (ICR), corrosion current, and corrosion potential are reported for various aC and

TiN thin films to characterize the contact resistance and corrosion resistance. The second study is etching of the previously deposited aC and TiN films in a HIPIMS system with a high-voltage cathode reversal, testing the possibility of recycling the BPP. The contact resistance and corrosion resistance are compared after the initial film deposition and then after etching of the initial film and redeposition on the same substrate.

8:45am **PS+TF-FrM-3 Evolution of Graphene Nanoflake Size and Morphology in Atmospheric Pressure Microwave Plasma**, ***Parker Hays***, *D. Patel, D. Qerimi,* University of Illinois at Urbana-Champaign; *M. Stowell,* LytEn; *D. Ruzic,* University of Illinois at Urbana-Champaign

Graphene was synthesized using an atmospheric pressure microwave plasma system, employing argon/nitrogen mixtures as carrier gases and methane as the carbon precursor. This study investigates the effects of varying methane flow rates and plasma power on graphene growth, including the role of gas temperature. The process involves the decomposition and subsequent reorganization of carbon radicals into graphene sheets. To collect the synthesized graphene, tungsten carbide rods were strategically positioned at three distinct points along the plasma column.

The variations in particle diameter were systematically analyzed using Dispersive Light Scattering (DLS) and Scanning Electron Microscopy (SEM). Results indicate that particle diameter generally decreases along the plasma column until reaching a critical power threshold. Beyond this threshold, the diameter increases, particularly at the middle collection port, suggesting the presence of an optimal "Goldilocks zone" for graphene growth. This zone, located at the juncture between the bulk plasma and its afterglow, exhibits a significant temperature gradient, potentially ideal for graphene formation.

Further, an increase in methane flow rate correspondingly reduced the particle diameter across all ports, attributed to enhanced plasma quenching effects. Conversely, an escalation in plasma power led to an increase in particle diameter, likely due to the extension of the plasma field.

These findings demonstrate that manipulating methane flow rates and plasma power can significantly influence graphene particle size, optimizing growth conditions within the identified Goldilocks zone. This study provides a deeper understanding of the thermodynamic and chemical mechanisms governing graphene synthesis in microwave plasma systems, offering a pathway to tailored graphene production for advanced material applications.

9:00am **PS+TF-FrM-4 Gentle Processing of Graphene and Diamond in a Low Temperature Magnetized Plasma**, ***Yevgeny Raitses***, Princeton Plasma Physics Laboratory; *F. Zhao,* Fermi Lab; *C. Pederson, K. Fu,* University of Washington; *A. Dogariu,* Princeton University

In this work, we present results of the use of a low temperature plasma in applied magnetic field for graphene hydrogenation and hydrogen passivation of diamond. The chemical functionalization of two-dimensional materials is an effective method for tailoring their electronical and chemical properties with encouraging applications in energy, catalysis and electronics. Experiments on graphene hydrogenation [1] revealed that with the applied magnetic field of 10-50 Gauss, a plasma generated by a DC-RF source of non-thermal electrons at a hydrogen pressure of about 10 mtorr is capable to achieve a high (~ 36%) hydrogen coverage without damage on monolayer graphene. Plasma measurements utilizing electrostatic probes for measurements of plasma properties, optical emission spectroscopy for characterization of plasma chemical composition and two-photon absorption laser-induced fluorescence (TALIF) for measurements of absolute hydrogen density revealed that with the applied magnetic field, the plasma density and the density of hydrogen atoms are much larger than without the magnetic field. The latter explains a high converge observed in the treated 2D material [1]. In more recent experiments, the same plasma source was applied for hydrogen passivation of diamond for quantum defect charge state control [2]. Measurements indicate that in this novel plasma treatment hydrogen terminates the surface with no observable damage to diamond.

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9:15am **PS+TF-FrM-5 A Plasma-Based Anodization Process for the Production of AlF_3 Layers**, ***Scott Walton***, *J. Murphy,* US Naval Research Laboratory; *L. Rodriguez de Marcos, J. Del Hoyo, M. Quijada,* NASA; *V. Wheeler, M. Sales, M. Meyer, D. Boris,* US Naval Research Laboratory

Efficient ultraviolet (UV) mirrors are essential components in space observatories for UV astronomy. Aluminum mirrors with fluoride-based protective layers are commonly the baseline UV coating technology; these mirrors have been proven to be stable, reliable, and with a long flight heritage. However, despite their acceptable optical performance, it is still insufficient for future large telescopes in which several reflections are required. Recently, a readily scalable, plasma-based passivation process was developed to produce a thin AlF3 layer on the surface of aluminum. The passivation process uses an electron beam generated plasma produced in a fluorine-containing background (SF6 or NF3), to simultaneously remove the native oxide layer while promoting the formation of an AlF3 layer with a tunable thickness. Interestingly, this process has the characteristics of classic aluminum anodization – either electrochemical or plasma – where oxygen is replaced by fluorine. The process takes advantage of the ability for electron beam driven plasmas produced in electronegative gas backgrounds to generate substantial densities of negative ions, which are utilized to grow the fluoride layer. In this presentation, we will discuss the process using operating parameter studies, plasma diagnostics, and materials characterization, with an eye on understanding the growth mechanisms and the potential for better process control. This work partially supported by the Naval Research Laboratory base program.

9:30am **PS+TF-FrM-6 One-Step Synthesis of Spatially Differentiated Crystalline Vanadium Oxide Coatings Using Atmospheric Pressure Dielectric Barrier Discharge**, ***Marie Brabant***, *A. Demaude, D. Petitjean, F. Reniers,* Université libre de Bruxelles, Belgium

Initially perceived as a limitation, the presence of inconsistencies in DBDs presented obstacles to achieving uniform plasma treatments and coatings. However, recent breakthroughs in immobilizing filaments within DBDs have demonstrated effective control over these irregularities.[1,2] This development has now enabled the deposition of innovative patterned inorganic coatings that were previously unexplored. Vanadium oxide coatings, in particular, hold promise for diverse applications, including catalysis,[3] memory compounds,[4] or as practical solutions for smart windows.[5]

This study introduces a pioneering method for locally depositing dense crystalline inorganic coatings (V_2O_5) without requiring annealing and utilizing atmospheric pressure DBDs, marking a significant advancement in the field. Vanadium oxide coatings with spatial variation were successfully deposited in a single step using an atmospheric pressure dielectric barrier discharge featuring immobilized filaments. Initial findings indicate fast deposition rates beneath the filament regions and low deposition rates between them. Moreover, differences in the oxidation states of vanadium beneath the filaments and between them were also observed, suggesting different reactivities.[6]

Through the incorporation of a patented inductive heating device into the reactor,[7,8] coupled with a pulsed signal, crystalline coatings were obtained by heating the substrate at 473 K, occasionally resulting in crystal needles measuring up to 50 µm in length. This crystallinity was confirmed by XRD analysis.

While further optimization is necessary to refine gas and reactive species distribution, this feasibility study demonstrates the potential for locally depositing crystalline coatings using a DBD with immobilized filaments and an appropriate substrate heating system, paving the way for new applications.

Acknowledgements

This work is funded by the FNRS (Belgian fund for research) under the Instream and Streamcoat projects.

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9:45am **PS+TF-FrM-7 Biofilm Decontamination in an Endoscope-Like Setup Using a Cold Atmospheric Plasma*, Juliette Zveny,*** Université libre de Bruxelles, Belgium*; F. Reniers, A. Remy,* Université Libre de Bruxelles, Belgium*; T. Serra,* université libre de Bruxelles, Belgium*; A. Bourgeois,* Erasme Hospital, Belgium*; A. Nonclercq, D. Lakhloufi, A. Botteaux,* université libre de Bruxelles, Belgium*; A. Delchambre,* Université Libre de Bruxelles, Belgium*; J. Deviere,* Erasme Hospital, Belgium

Endoscopes are essential medical devices used to detect, prevent and cure many diseases. Well-established cleaning and decontamination procedures allow them to be used safely on multiple patients every day. However, cases of cross-contamination still occur, demonstrating that the decontamination process is flawed.[1] Here, we propose a novel decontamination method using an Ar/H_2O Cold Atmospheric Plasma (CAP).

In this research, we investigate the effect of CAP not only on bacteria, but also on biofilm.Biofilm is a matrix made by bacteria to increase their resistance to external stress.[2] Pseudomonas aeruginosa biofilms were grown during 24 hours in a PTFE tube mimicking the operating channel of an endoscope before being subjected to plasma treatment. The plasma was generated in a DBD setup with the high voltage applied between a metal wire passing through the contaminated tube and a metal mesh surrounding the tube.

The decontamination process consisted of a 30 min plasma in a water-saturated argon atmosphere. The chemical activity of the discharge was optimized by the presence of water, which allowed the production of hydroxyl radicals (OH) and hydrogen peroxide (H_2O_2), powerful oxidant species. Other parameters, such as the voltage, made it possible to increase the concentration of these species without increasing the power.

Plasma treatments showed effective decontamination capacities, with no bacteria found in the tube after regrowth for various treatment times (5 to 30min). It also shows promising results in terms of biofilm destruction, with up to 79% of the original biofilm destroyed. The biofilm destruction is dependent on the position inside the tube as well as on its own humidity. OES measurements also highlight the voltage dependency on OH radical formation and biofilm destruction.

Acknowledgements:

This work is funded by the ARC project COSMIC (ULB) and by the Cremer Foundation.

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10:00am **PS+TF-FrM-8 Nonthermal Plasma Jet Integrated Aerosol-Based 3D Printing with Machine Learning Optimization*, Jinyu Yang*,** *Y. Du, K. Song, Q. Jiang, Y. Zhang, D. Go,* University of Notre Dame

Aerosol-based printing has emerged as a versatile technique to fabricate functional devices with complex structures, offering high throughput and microscale resolution, along with capabilities unattainable with traditional approaches. Despite these promises, the printing of conductive films often requires post-printing sintering to remove surfactants from the nanoparticle-containing inks and promote the sintering and densification to form a continuous film with desired electrical conductivity, which conventionally demands thermal processing at elevated temperatures. Herein, we report a novel aerosol jet printing method that integrates a nonthermal, atmospheric pressure plasma jet to enable *in-situ* sintering during aerosol deposition. The impacts of various processing parameters on printing quality and *in-situ* sintering efficiency are investigated. A machine learning algorithm is incorporated to provide online, real-time defect detection and parameter control, enhancing the yield of high-quality films via automatic *in-situ* compensation whenever a region-specific anomaly is detected. Our method achieves low temperature sintering of silver nanoparticles with electrical conductivities comparable with those sintered through other plasma treatment approaches. Because the films require no post processing, the overall manufacturing time can be reduced by more than tenfold. This method holds significant potential for technological advances in printed electronics, wearable devices, and biomanufacturing.

Thin Films
Room 115 - Session TF1+EM-FrM
Thin Films for Microelectronics III: Wide Band Gap Materials

Moderators: Jessica Kachian, Kokusai Semiconductor Equipment Corporation, **Virginia Wheeler**, U.S. Naval Research Laboratory

8:15am **TF1+EM-FrM-1 Interlayer Engineering of Heterostructure Thermal Boundary Resistance of Power Device Heat Spreader***, Y. Jo, T. Hwang,* ***Kyeongjae Cho,*** University of Texas at Dallas **INVITED**

The needs for high power electronic devices are expanding for diverse applications including power conversion, smart grid, renewable energy generation and storage systems. The power capacity of devices is correlated to the bandgap of the semiconductors, and the current GaN power devices are expected to evolve to more powerful devices with ultra-wide bandgap semiconductors (e.g., b-Ga2O3, diamond, AlN, c-BN) in the future. As the power capacity of a device increases, the increasing waste heat generated by the operation must be removed efficiently and maintain the device temperature sufficiently low to avoid accelerated degradation and premature failure of the devices. However, even the performance of current GaN power device is limited by the capacity of waste heat removal at the device level from the hot spots. Specifically, the thermal resistance along the heat transport pathway from the GaN device hot spots to an adjacent heat spreader (e.g., diamond or AlN) is dominated by the thermal boundary resistance (TBR) of the heterostructure interfaces. To enable the full potential performance of GaN power devices, it is critically important to optimize the GaN/diamond TBR well below the previously reported values which are larger than the classically known limit of ~3 m^2K/GW based on the diffuse mismatch model (DMM) study of phonon transport at the heterostructure interfaces. In this talk, we will discuss the role of nanoscale interlayers at the heterostructure interfaces and demonstrate that the interlayer phonon engineering can enable novel phonon transport mechanisms at nanoscale leading to TBR values lower than the classical DMM limit. We envision applying the nanophononics design of interlayers to address the thermal management challenges of high-power devices.

This work was supported by DARPA Sponsored Special Projects (DSSP) in 2021 and 2022 and is currently supported by DARPA Technologies for Heat Removal in Electronics at the Device Scale (HTREADS) program.

8:45am **TF1+EM-FrM-3 Characterization of Defects in AlN Using Deep Ultraviolet Photoluminescence*, Virginia Wheeler,*** *N. Nepal, M. Hardy, A. Lang,* Naval Research Laboratory*; J. Hart,* Nova Research Inc*; B. Downey, D. Meyer,* Naval Research Laboratory

AlN is being explored as an ultrawide bandgap material that offers the combined possibility of higher voltage handling and better thermal management than current semiconductor technologies such as GaN, SiC, and Si. However, realizing the full potential of this material in electronic device applications requires the ability to tailor the electrical conductivity in active AlN layers through impurity doping. Due to the large bandgap and lower formation energy of native point defects, which serves as carrier compensating centers, impurity doping in AlN has been challenging and lacking in reproducibility. Deep ultraviolet photoluminescence (DUVPL) is a crucial tool to identifying near-band edge emission and radiative point defects within ultrawide bandgap materials. In this work, we use DUVPL to identify and correlate defect and band edge emission intensities with AlN substrates and films deposited by molecular beam epitaxy (MBE) to point towards approaches to achieving electrical conductivity for device applications.

Si-doped AlN films, ~300-500 nm thick, were deposited by plasma-assisted MBE on both AlN/sapphire templates and bulk AlN substrates from different vendors using a metal modulated epitaxy approach. All AlN substrates underwent an *ex-situ* chemical clean and *in-situ* Al-absorption and desorption technique to create an abrupt, pristine, oxygen-free growth interface. Resulting films were characterized using DUVPL, x-ray diffraction (XRD), atomic force microscopy (AFM) and van der Pauw resistivity measurements. Cross-sectional transmission electron microscopy (TEM) measurements were carried out on selected samples along (10-10) and (11-20) orientations to assess the epitaxial material quality and defect density.

DUVPL measurements of MBE AlN layers, using above bandgap excitation (at 6.458 eV), show that unintentionally-doped AlN films have strong band-edge emission and no impurity bands. After Si doping, an impurity band appears near 3.67 eV related to an Al-vacancy Si-complex and the band-edge emission at 6.03 eV decreases. Van der Pauw resistivity measurements show that conductive AlN:Si films can be obtained on all substrates, but minimal changes in resistivity result from varying growth parameters further. For AlN layers grown under similar conditions, conductive AlN films have lower intensity impurity bands. Results correlating DUVPL, XRD, AFM, TEM and resistivity measurements for the full parameter space will be discussed.

9:00am **TF1+EM-FrM-4 Ultrathin Tantalum Films for Silicon Carbide Schottky Barrier Diode***, **Renato Beraldo**, R. Reigota Cesar, J. Alexandre Diniz,* Center for Semiconductor Components and Nanotechnology - CCSNano, Brazil

The first device based on SiC released was a Schottky barrier diode (SBD), and device is basically a junction of a semiconductor and a particular metal capable of providing a rectifier contact. Therefore, instead of focusing only on the work function of the elements, it is important to pay attention to the quality of the interface between metal and semiconductor, for example, inhomogeneous levels, defects, impurities and morphology, which can cause interface states and change the factor of ideality (ideal is 1). Since then, ways of creating surface arrangements associated with better quality have been employed, including metallization techniques, annealing treatments, types of metals, geometric arrangements, and even the addition of tiny oxides, where some of these Applications can adjust SBH values and improve reliability resource results.

Among many metallization techniques, studies using ultrathin films yielded high quality junctions employing Ni onto Si and W, Ti onto SiC. So then, based on these results, the motivation of this work was the selection of tantalum to be the metal with this metallization technique, due to its low work function that could provide lower resistance of SBH and its refractory properties which could afford elevated temperature without affecting the device performance.

Initially, a double side polished SiC wafer n-type of 350 µm thick (0.015~0.028 Ω.cm) with drift layer of 3x1015 cm-3 dopants and 30 µm thick was selected. The samples were cleaned with 10 minutes in piranha bath and nitric acid 30% at 50 ºC. After the cleaning process, 2 nm of tantalum was deposited by RF sputtering at the top of the samples to form Schottky contact and then, rapid thermal annealed performed from 500 to 700°C under 50°C intervals. Then 100 nm of aluminum was deposited by thermal evaporation to provide electric contact for test probes. To create the ohmic contact, 100 nm of nickel was deposited by sputtering without any thermal treatment. The samples were diced in 1 cm2 and followed by lithographic pattern with squares of 30 µm side.

Each device was submitted to IxV curves to check the current response, leakage current under reverse bias, SBH, and ideality factor. At Fig. 1 it is possible to verify that the annealing treatment yielded the difference among the annealing treatments. At the Fig. 1, the best result was related to the 650ºC which showed lower values of leakage current and value of SBH around 0.74 eV and ideality factor of 1, resulting in a low resistance device addressed to power devices, combined with the lowest leakage current, as shown in Fig. 2.

9:15am **TF1+EM-FrM-5 Plasma Enhanced Atomic Layer Deposition of Hydrogen Free In_2O_3 Thin Films with High Charge Carrier Mobility***, **Sudipta Mondal**, I. Campbell, A. Bol,* University of Michigan, Ann Arbor

In_2O_3 has recently emerged as an alternative channel material for field effect transistors (FETs), owing to its exceptional carrier mobility preservation even when scaled down to ultra-thin layers below 10 nm. Despite the superior performance of In_2O_3-based FETs, understanding the underlying operation mechanisms is incomplete, particularly concerning the impact of native defects and doping. Hydrogen dopants in metal oxide films are often responsible for increased Hall mobility, albeit at the detriment of device stability. Herein, we have used plasma-enhanced atomic layer deposition (PEALD) to deposit highly uniform and conformal In_2O_3 thin films. A β-diketonate indium precursor tris(2,2,6,6-tetramethyl-3,5-heptanedionato) indium-(III), which is stable over a large temperature range was used as the indium source. O_2 plasma was selected for oxygen incorporation instead of hydrogen-containing precursors like H_2O to prevent unintentional hydrogen doping, while still aiming for high carrier mobility. Saturation behaviour for the PEALD process was studied using in-situ spectroscopic ellipsometry and indicated a wide ALD window from 150^{o}C to 500^{o}C. Our optimized process achieves a growth rate of 0.14 Å/cycle at 150^{o}C, and 0.29 Å/cycle at 500^{o}C. The In_2O_3 films manifest in a polycrystalline Bixbyite cubic phase, as confirmed by grazing incidence X-ray diffraction (GIXRD). The chemical composition of the films was investigated using X-ray photoelectron spectroscopy (XPS), which revealed a rising number of oxygen vacancies with increasing deposition temperature. Diverse analytical methods, including UV-vis spectroscopy, scanning electron microscopy (SEM), and Hall measurements, were employed to elucidate the influence of oxygen vacancies on the film properties. Our n-type In_2O_3 films showed a Hall mobility value of 84.1 cm^2/V-s at a deposition temperature of 150^{o}C, which is among the highest reported for ALD In_2O_3 thin films, making them an ideal candidate as a channel material in FET devices. Through Elastic Recoil Detection Analysis (ERDA), we have excluded the presence of hydrogen dopants by comparing the relative hydrogen concentration in the substrate and the sample, (detection limit ≥0.01 atomic %), cementing the role of oxygen vacancies as the principal contributor to the exceptional electrical behaviour in our films. Moreover, we explored post-deposition annealing in air and argon atmospheres as a strategy to modulate oxygen vacancies and, by extension, the electrical properties of the films. We observed that air annealing increases resistivity by eliminating oxygen vacancies, while vacuum annealing enhances conductivity by creating oxygen vacancies.

9:30am **TF1+EM-FrM-6 Epitaxial Integration of Transition-Metal Nitrides with Cubic Gallium Nitride***, **Zachery Cresswell**, N. Fessler, T. Garrett, K. Vallejo, B. May,* Idaho National Laboratory

GaN is ubiquitous in the optoelectronics industry in its thermodynamically stable wurtzite structure, but it also has a metastable zinc blende allotrope that is less explored and more difficult to synthesize. One of the potential advantages of cubic-GaN (c-GaN) is the simplified interfacial symmetry with the other cubic transition metal nitrides, which are of interest for an assortment of applications requiring high chemical and thermal stability, high hardness, superconductivity, or plasmonic properties. The shared cubic symmetry would allow for easier integration of the nitrides with a wide-bandgap semiconductor.

This work will discuss the synthesis of epitaxial c-GaN on 3C-SiC substrates and its integration with known superconducting nitrides via molecular beam epitaxy. The hexagonal-free nature of the c-GaN, and the epitaxial relationship of it and the transition metal nitrides, are confirmed via *in-situ* reflection high energy electron diffraction, *ex-situ* X-ray diffraction, photoluminescence, and transition electron microscopy. The electrical transport of the transition metal nitrides grown on c-GaN(001) is compared to growth directly on 3C-SiC(001) and c-plane hexagonal GaN. Epitaxial synthesis of cubic wide-bandgap and superconducting metallic nitrides under similar growth conditions opens a new world of possibilities in band engineering, as well as the ability to create new device structures for areas such as metamaterials, quantum computing, and condensed matter physics.

9:45am **TF1+EM-FrM-7 Comparison of AlScN Thin Films Grown via Pulsed Laser Deposition and Sputtering***, **John Wellington-Johnson**,* Georgia Institute of Technology

$Al_xSc_{1-x}N$ (AlScN) is a promising material for piezoelectric micro-electro-mechanical systems (MEMS) applications, due to its high coupling coefficient (k_t^2 > 15.5%) , large piezoelectric coefficient (>27 pC/N), and CMOS compatibility [1,2]. However, large variability in film crystallinity, orientation, composition, and grain morphology still limit the full potential of AlScN [2]. The majority of literature focuses on the sputtering growth on AlScN but and there is great variability in the film quality, with multiple deposition parameters influencing the resultant film composition, morphology, and crystallinity - there are limited reports on the impact of pulsed laser deposition on AlScN film quality. This presentation will compare the impact of thin film growth by sputtering and PLD to determine the impact on the resultant AlScN films' crystalline, compositional, and morphological features.

AlScN thin films were deposited on (111) platinized silicon by PLD and RF or DC sputtering. In PLD, thin films are deposited from a single stoichiometric $Al_{70}Sc_{30}N$ target, whereas two independent AlN and Sc targets are used in sputtering. X-ray reflectivity (XRR) and diffraction (XRD) studies are used to characterize film thickness and phase. XRD scans reveal the films maintain the desired (0002) orientation over a range of temperatures and laser fluences. Compositional analysis and depth profiling reveals the nature of surface and bulk oxygen through the film, with discussions on the differing oxidation states and bonding environments of the O1s spectra, with respect to each growth method. Grain size, surface roughness, and surface morphology of the films will also be presented through SEM and AFM studies – with R_a ranging from 1.3 to 5 nm. These results illustrate and compare the PLD growth of c-axis oriented AlScN thin films under CMOS conditions.

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10:00am **TF1+EM-FrM-8 Exploring the Impact of [Si-C] and [N=C] Bonds in SiCN Films by First Principles Calculation: A Study of Composition, Structure, and Properties***, **Tsung-Hsuan Yang,*** Tokyo Electron America, Inc.*; G. Hwang,* University of Texas at Austin*; P. Ventzek, J. Zhao,* Tokyo Electron America, Inc.

Silicon carbon nitride (SiCN) is a dielectric material featuring a variety of desirable properties, including thermal stability, chemical resistance, and materials strength. It has been found to have better materials properties than silicon nitride (Si_3N_4) due to its potential for controlling the element compositions and microstructure. However, the relationship between SiCN microstructure and materials properties is not well understood. This simulation study aims to bridge the gap by correlating the bonding environment in SiCN with materials properties, specifically by investigating the effect of adding [Si-C] or [N=C] bonds to SiN film. We begin by constructing amorphous SiCN in two ways: replacing Si with C to create [N=C] bonds or replacing N with C to create [Si-C] bonds. The resulting films were annealed at 500K to optimize geometry and passivate defective sites with hydrogens. A wide range of Si, N and C compositions (e.g., Si_3N_4, SiC, $Si_2N_4C_1$) and different C bonding environments were examined. The film stability was tested, and properties such as dielectric constant, refractive index, band gap, bulk modulus, H content, and bond densities were calculated. The study successfully demonstrates how [N=C] and [Si-C] bonds modify the materials properties of SiCN film, providing guidelines for tailoring the materials properties of SiCN.

Thin Films
Room 115 - Session TF2-FrM
Thin Films: Characterization

Moderators: Mark Losego, Georgia Institute of Technology, **Virginia Wheeler**, U.S. Naval Research Laboratory

10:30am **TF2-FrM-10 Variable-Angle, Spectroscopic Ellipsometry Studies of the Repeated Application of First Contact Polymers on Optical Surfaces***, **Joshua Vawdrey,*** Brigham Young University*; J. Hamilton,* University of Wisconsin, Platteville*; D. Allred,* Brigham Young University

First Contact Polymer™ (FCP) is an adhesion-based, cleaning polymer that has been shown to remove molecular and particulate contamination from surfaces. Applying, allowing to dry, and then peeling off a layer of FCP from a contaminated surface embeds and removes contaminants. While a single peel-off has been observed to be effective at removing both particulate and molecular contaminants, the effect of consecutive fresh applications and peel-offs on the same surface has not been extensively studied. This is important since FCP is used to protect optical surface in storage. Using variable-angle, spectroscopic ellipsometric (VASE) data, modeled with J.A. Woollam Inc. software, CompleteEase, we addressed the questions: can surfaces be cleaned multiple times recovering the same clean surface each time? And what formulations are suitable for hygroscopic materials like lithium fluoride? One set of thin-film materials studied were three that are important materials in silicon microelectronics: native oxide on "bare" silicon wafer pieces, CVD silicon nitride on silicon wafers, and thermal silicon dioxide on silicon wafers. In addition, surfaces important in thin-film optics including far ultraviolet (FUV) were examined. These were metal fluoride thin films on evaporated aluminum. At each iteration in the study, we removed the layer of FCP coating each sample, measured the surface at several different spots with VASE, reapplied FCP and stored the samples for a designated time. Control samples, which received no FCP but were stored with the others, were also measured iteratively. We observed a reduction in the top-layer thickness of both silicon and CVD silicon nitride on silicon samples after cleaning impure solvent residue off the surface- We interpret this as FCP can effectively remove physisorbed materials from such surfaces yielding atomically clean surface in the absence of can be absorbed layers. We observed that the apparent native oxide layer on both FCP-coated samples and control samples increased with time. This could be due to the deposition of adventitious carbon from the environment. There is a slight increase--about an eighth of an angstrom per repeated peel-off, in the apparent top-layer thickness of the native oxide on Si samples. Cleaning fluorides proved to be more challenging. This is due to affinity of some fluorides particularly LiF to water. We determined condition under which some fluorides can be effectively cleaned without trapping water. Coatings suitable for long-term storage of fluorides are still under investigation.

10:45am **TF2-FrM-11 EnviroMETROS – A Novel Surface and Multilayer Thin Film Analysis Tool***, **Paul Dietrich**, F. Mirabella, S. Boetcher, K. Kunze, O. Schaff, A. Thissen,* SPECS Surface Nano Analysis GmbH, Germany

The new EnviroMETROS series transforms the realm of surface hybrid metrology by employing the key techniques of parallel detection angle resolved XPS (PARXPS) and multi-wavelength excitation. This method utilizes variable photon energies and emission angles operating under diverse environmental conditions for conducting chemical analyses of thin films and bulk materials. LEIS facilitates high surface sensitivity, while electronic characterization can be enhanced with UPS, IPES, and REELS. Integrated Raman and/or IR spectroscopy provide structural information, whereas XPS mapping and SEM/SAM contribute to elemental surface maps correlated with morphology.

The relevance of ultrathin films and 2D materials in modern devices is continuously increasing, prompting a growing interest in the chemical analysis of these multilayer systems and their surfaces. A thorough characterization of stoichiometries, composition, and depth distribution of elements is crucial. The novel EnviroMETROS series serves as an ideal tool for routine analysis in this research and development field. It combines large sample and wafer handling with a photoelectron spectrometer offering variable information depth. When combined with optical and other analytical techniques, it enables depth-dependent composition analysis with unparalleled precision, reliability, and repeatability.

11:00am **TF2-FrM-12 Passivation of Indium Phosphide Substrate Evaluated by Atomic Force Microscopy***, **Fabiano Borges,*** Federal Institute of Sao Paulo, Brazil*; C. Almeida,* PUC-Rio, LabSem, Brazil*; A. Silva,* Unicamp, CCS, Brazil*; O. Berenguel, C. Costa,* CNPEM, LNNano, Brazil*; G. Vieira,* IEAv, Brazil*; J. Diniz,* Unicamp, CCS, Brazil

Passivation involves coating a material to make it passive, i.e., less affected by the environment. In this study, passivation is achieved by depositing an aluminium oxide layer with prior surface treatment. Four surface treatments are considered: oxidation only (O), nitriding only (N), oxidation followed by nitriding (ON), and nitriding followed by oxidation (NO). An InP substrate is heated and exposed to an environment enriched with oxygen and/or nitrogen to form a thin film over the InP surface. Following this, a 20nm thick layer of aluminium oxide is deposited using atomic layer deposition (ALD). Thus, six different samples were generated for analysis: four with surface treatments, one of pure InP without any added thin film, and one of InP with only an aluminium oxide layer as the control sample for reference. This process presumably enables electricity to reliably penetrate the conducting InP below the surface while overcoming the surface states that hinder electrical conduction in the semiconducting layers. Different techniques such as Photoluminescence Spectroscopy, Atomic Force Microscopy, Electrostatic Force Microscopy, and X-ray Photoelectron Spectroscopy can be used for evaluating these treatments' effectiveness. The simplest one, analysing AFM images [1] alongside their RMS roughness values [2], reveals that samples with lower RMS roughness also possess fewer defects at their surfaces [3]. By defining the RMS roughness value of the control sample as the reference, all other values are lower: pure InP has a 15% lower RMS roughness, N has 10%, O has 20%, NO has 15%, and ON 10%. This suggests that the O sample is the smoothest and likely possesses the lowest surface defect density.

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Acknowledgments

This research is supported financially by IFSP (Federal Institute of Education, Science, and Technology of São Paulo), FINEP e CNPq. Research supported by LNNano – Brazilian Nanotechnology National Laboratory (CNPEM/MCTI) during the use of the Atomic Force Microscopy and Synthesis (MFAS) open access facility. The InP substrate were kindly supplied by LabSem of PUC-

Rio. The author also thanks the support of the Instituto de Estudos Avançados of the Brazilian Air Force.

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