Monday Morning, November 4, 2024

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 ± 0.1 for the selective SiCO layer which is 1.8 times lower compared to selectively deposited of AlOx with k ~ 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.

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

TEL Technology Center, America, LLC, 255 Fuller Road, suite 214, Albany, NY 12203

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.

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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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Quantum Science and Technology Mini-Symposium
Room 123 - Session QS1+EM+MN+PS-MoA

Materials + Devices for Quantum Systems

Moderators: Parag Banerjee, University of Central Florida, **Jaesung Lee**, University of Central Florida

1:30pm **QS1+EM+MN+PS-MoA-1 Elastic Layered Quantum Materials***, **Jiun-Haw Chu**,* University of Washington **INVITED**

Recently elastic strain has emerged as a powerful tool for probing and controlling quantum materials. By changing chemical bond lengths, elastic strain can modulate electronic structure up to very high energy scale. Additionally, as a second rank tensor, strain enables access to various instabilities associated with different symmetry channels. In this talk, I will discuss several examples of the application of strain to unconventional electronic orderings in van der Waals layered materials, including zigzag antiferromagnetism, charge density waves and excitonic insulators.

2:00pm **QS1+EM+MN+PS-MoA-3 Controllable Extended Defect States in Topological Insulators and Weyl Semimetals***, **Eklavya Thareja**, J. Gayles,* University of South Florida*; I. Vekhter,* Louisiana State University

Over the past decade study of topological materials has emerged as one of the most active areas in condensed matter physics, owing to a wide range of their proposed applications ranging from quantum computing to spintronics. What sets them apart from the materials currently used to build information technology is their robustness to disorder. However, in addition to the immunity of their electronic states against disorder, one needs ways to control the properties of these electronic states in these materials. We show that extended defects such as line defects and planar defects host localized states in Topological Insulators and Weyl Semimetals, which are two common topological materials. These localized states can be manipulated by controlling the scattering at the defects, for example, by using an external magnetic field. This leads to controllable spin accumulation and non-dissipative currents near the defects, due spin-momentum locking. These results bring us closer to functional applications.

2:15pm **QS1+EM+MN+PS-MoA-4 Topological Interfacial State in One-Dimensional h-BN Phononic Waveguide***, Y. Wang, **Sanchaya Pandit**,* University of Nebraska - Lincoln

Artificial topological structures have gained considerable research attention in the fields of photonics, electronics, mechanics, acoustics, and many others, as they promise robust propagation without loss along the edges and interfaces. In this work, we explored the topological states in one-dimensional (1D) phononic waveguides empowered by hexagonal boron nitride (h-BN), a hallmark two-dimensional (2D) material with robust mechanical properties that can support phonon propagation in high frequency regime. First, degenerate trivial and nontrivial topological structures were designed based on the Su-Schrieffer-Heeger (SSH) model. The dispersion engineering was then performed to match the passbands and bandgaps for these two topological structures through optimizing the geometric parameters of the unit cells. An interfacial state emerged when connecting these two sets of unit cells together and forming the 1D waveguide. The topological nature of this interfacial state, immune to structural and material parameter perturbation, was verified with the variation of strain and thickness in the waveguide. The phononic topological state studied here can be further coupled with defect-related quantum emitters in h-BN, opening the door for next-generation hybrid optomechanical circuits.

2:30pm **QS1+EM+MN+PS-MoA-5 Scanning Nano-Optical Imaging of Quantum Materials***, **Guangxin Ni**,* Florida State University

Scanning near-field Nano-Optical imaging is an invaluable resource for exploring new physics of novel quantum materials. Surface plasmon polaritons and other forms of hybrid light-matter polaritons provide new opportunities for advancing this line of inquiry. In particular, nano-polaritonic images obtained with modern scanning nano-infrared tools grant us access into regions of the dispersion relations of various excitations beyond what is attainable with conventional optics. I will discuss this emerging direction of research with two examples from 2D layered quantum materials.

2:45pm **QS1+EM+MN+PS-MoA-6 Engineering of Erbium-Implanted Lithium Niobate Films for Integrated Quantum Applications***, **Souryaya Dutta**,* College of Nanotechnology, Science, and Engineering (CNSE), University at Albany*; A. Kaloyeros, S. Gallis,* College of Nanotechnology, Science, and Engineering (CNSE), University at Albany (UAlbany)

Rare-earth-doped materials have garnered significant attention as material platforms in emerging quantum information and integrated photonic technologies. Concurrently, advances in its nanofabrication processes have unleashed thin film lithium niobate (LN), $LiNbO_3$, as a leading force of research in these technologies, encompassing many outstanding properties in a single material. Leveraging the scalability of ion implantation to integrate rare-earth erbium (Er^{3+}), which emits at 1532 nm, into thin film lithium niobate can enable a plethora of exciting photonic and quantum technologies operating in the telecom C-band. Many of these technologies also rely on coupling via polarization-sensitive photonic structures such as waveguides and optical nanocavities, necessitating fundamental material studies.

Toward this goal, we have conducted an extensive study on the role of implantation and post-implantation processing in minimizing implantation-induced defectivity in *x*-cut thin film LN. By leveraging this, we have demonstrated an ensemble optical linewidth of ~140 GHz of the Er emission at 77 K. Our demonstration showcases the effectiveness of our ion implantation engineering in producing cutting-edge Er emission linewidth in thin film LN at higher temperatures compared to values reported for diffusion-doped bulk materials at liquid helium temperatures (~3 K). Furthermore, we show that the Er photoluminescence (PL) is highly polarized perpendicular to the *x*-cut LN *c*-axis through a systematic and combinational PL and high-resolution transmission electron microscopy (HRTEM) study. These results indicate that using Er rare-earth emitters in thin film LN, along with their polarization characteristics and related ion implantation engineering, presents a promising opportunity to produce highly luminescent Er-doped LN integrated photonic devices for nanophotonic and quantum applications at telecom wavelengths.

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)

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

2D Materials by Design: Intercalation of Cr or Mn between two 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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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 $6\sqrt{3}$ buffer layer that forms during growth on SiC(0001) remains on the SiC substrate. Consequently, if there are regions of exposed $6\sqrt{3}$ buffer layer in the as-grown MEG on SiC, AFM shows that there are corresponding gaps in the transferred graphene film where the areas of exposed buffer layer do not transfer. The $6\sqrt{3}$ buffer layer is not present in QFBEG due to the hydrogen-intercalation process. It is found that the same Ni sputtering conditions that led to uniform exfoliation and transfer of MEG result in micron-scale tears in the Ni/QFBEG film. By lowering the strain energy in the sputtered Ni film, these tears can be reduced or eliminated.

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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)

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 $La_{1-x}Sr_xCoO_{3-d}$ (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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[2] D. Winge, M. Borgström, E. Lind, and A. Mikkelsen, “Artificial nanophotonic neuron with internal memory for biologically inspired and reservoir network computing”*, Neuromorph. Comput. Eng.*, vol. 3, no. 034011, 2023.

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.

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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).

2D Materials
Room 122 - Session 2D+EM+MI+QS-WeM
2D Materials: Heterostructures, Twistronics, and Proximity Effects

Moderators: Aaron Bostwick, Advanced Light Source, Lawrence Berkeley National Laboratory, **Tiancong Zhu**, Purdue University

8:00am **2D+EM+MI+QS-WeM-1 Van der Waals Semiconductors: From Stacking-Controlled Crystals to Unconventional Heterostructures***, **Peter Sutter**, E. Sutter,* University of Nebraska - Lincoln **INVITED**

2D materials have attracted broad interest due to novel properties that arise in atomically thin crystals. As interesting scientifically and important technologically, but much less explored are van der Waals (vdW) crystals that, assembled from 2D building blocks, lie between a monolayer and the bulk. In this regime, phenomena such as phase separation, transformations between crystal polymorphs, and competition between different stacking registries provide unprecedented opportunities for controlling morphology, interface formation, and novel degrees of freedom such as interlayer twist. But going beyond a single layer also poses significant challenges, both due to the diversity of the possible few-layer structures and the difficulty of probing functionality such as optoelectronics and ferroics at the relevant length scales.

Here, we discuss our recent research that addresses these challenges focusing on group IVA chalcogenides, an emerging class of anisotropic layered semiconductors promising for energy conversion, optoelectronics, and information processing. Advanced *in-situ* microscopy provides insights into the growth process, interlayer twisting,and emerging functionality such as stacking-controlled ferroelectricity. Nanometer-scale electron excited spectroscopy identifies photonic light-matter hybrid states and reveals anisotropic and valley-selective charge carrier flows across interfaces in heterostructures. Our results highlight the rich sets of materials architectures and functionalities that can be realized in van der Waals crystals and heterostructures beyond the 2D limit.

8:30am **2D+EM+MI+QS-WeM-3 Deterministic Assembly, Transfer, and Flipping of 2D Materials Using Tunable Polymer Films***, **Jeffrey J. Schwartz**, S. Le,* University of Maryland, College Park*; K. Grutter, A. Hanbicki, A. Friedman,* Laboratory for Physical Sciences

Assembly of two-dimensional (2D) materials into van der Waals heterostructures is a crucial step in creating precisely engineered nanoscale and quantum devices for use in a wide variety of spintronic, electronic, and other applications. Numerous strategies exist to pick-up, stack, transfer, and even flip over these atomically thin structures. One popular strategy leverages the ability to tune the adhesion between a polymer stamp and 2D sheets to pick-up, stack, and release structures at different temperatures. Although relatively easy to implement, this technique is tedious to perform and has a low throughput. Here, we demonstrate a significant improvement to a deterministic, all-dry, polymer-assisted transfer technique using polyvinyl chloride (PVC) thin films to manipulate 2D materials and to fabricate devices. We construct stamps from pairs of commercially available PVC films that controllably pick-up and release 2D sheets within known, overlapping temperature ranges. These mechanically durable stamps can be produced quickly and without the time-consuming preparation and annealing steps required by most other commonly used polymers. Importantly, these stamps not only facilitate deterministic transfer of 2D materials, but they also enable polymer-to-polymer transfer (e.g., between separate stamps) and flipping of material stacks to create inverted heterostructures that are important for many applications, including scanning tunneling microscopy measurements. We characterize the thermal transition properties of the PVC films employed here as well as assay the cleanliness and performance of devices produced using this technique. These improvements enable rapid production of 2D devices with fewer interactions required by the operator, which is especially significant when working in controlled environments (e.g., glovebox) or in remote or autonomously controlled contexts.

8:45am **2D+EM+MI+QS-WeM-4 Cleaning of Low-Dimensionality Materials: Challenge and Solutions***, **Jean-Francois de Marneffe**, P. Wyndaele, M. Timmermans, C. Cunha,* IMEC, Belgium*; B. Canto, Z. Wang,* AMO GmbH, Aachen, Germany*; R. Slaets, G. He, I. Asselberghs, C. J. Lockhart de la Rosa, G. Sankar Kar, C. Merckling, S. De Gendt,* IMEC, Belgium

Over the last few years, significant efforts have been made in exploring low-dimensionality materials such as single layer Graphene (SLG), transition metal dichalcogenides (TMDCs) and carbon nanotubes (CNTs), for a wide range of applications covering beyond CMOS logic, EUV pellicles, photonics, and sensing (amongst others). Due to their intrinsic 2D or 1D nature, these materials are highly sensitive to processing damage leading to stoichiometric changes or crystalline defects. Among the many manufacturing steps required for building devices, the cleaning of these systems is an absolute requirement and a bottleneck. Typically, during processing, residual polymers or carbon of ambient origin, do contaminate the surface leading to nanometric deposits that change the intrinsic transport/optical properties of the materials, and cause parasitic dielectric drift or high contact resistance. Wet cleaning, using organic solvents, is a mainstream approach, which proves to be inefficient for irreversibly physically adsorbed polymer residues. In this paper, we explore dry cleaning approaches, based on plasma treatment and UV cure. Plasma-based cleaning proves to be very efficient but leads to material damage, which can be minimized by tuning the average ion energy, the processing temperature, the plasma chemistry or adding a post-cleaning restoration step. For TMDCs, damage consist essentially in the creation of chalcogen vacancies, which lead to metal oxidation upon ambient exposure. For Graphene and CNTs, damage consist in carbon vacancies, causing lattice distortions, oxidation and ultimately a dramatic change of the material's transport properties. Part of this presentation will explore the use of UV cure, which is a known method for cleaning polymers from semiconductor surfaces.

9:00am **2D+EM+MI+QS-WeM-5 Spin-Valley Physics in Mixed-Dimensional Van Der Waals Heterostructures***, **Vikram Deshpande**,* University of Utah **INVITED**

Spin-valley physics has become ubiquitous in 2D materials-based van der Waals (vdW) heterostructures, particularly those hosting flat bands, wherein various ground states with spin-valley character including magnetic, insulating and superconducting states have been observed. On the other hand, mixed dimensional vdW heterostructures, such as those between 2D and 1D materials have been less explored for intricate spin-valley physics. The reduced phase space for scattering in 1D in particular might lead to qualitatively different phenomena. We are guided by our studies of ultraclean carbon nanotube quantum dots wherein we have observed subtle effects from the degeneracy lifting between the speeds of right- and left-moving electrons within a given Dirac cone or valley. Bound states can be purely fast-moving or purely slow-moving, giving rise to incommensurate energy level spacings and a vernier spectrum. Using quantum interferometry [1] and Coulomb blockade spectroscopy [2] of such ultraclean carbon nanotube quantum dots, we have found evidence for this vernier spectrum. The addition-energy spectrum of the quantum dots reveals an energy-level structure that oscillates between aligned and misaligned energy levels. Our data find that the fast- and slow-moving bound states hybridize at certain gate voltages. We extend existing theory to show that our experiment probes the degree of isospin polarization/hybridization of the various quantum states probed in our system. As a result, gate-voltage tuning can select states with varying degrees of hybridization, suggesting numerous applications based on accessing this isospin degree of freedom in conjunction with 2D materials in the form of mixed dimensional vdW heterostructures. We have fabricated prototypical mixed dimensional vdW heterostructures between carbon nanotubes and 2D materials and extended our measurements to these structures. I will discuss our recent and ongoing work studying spin-valley physics in such systems.

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9:30am **2D+EM+MI+QS-WeM-7 Exploring Incommensurate Lattice Modulations in BSCCO van der Waals Heterostructures: Implications for Q-Bit Development***, **Patryk Wasik**,* Brookhaven National Laboratory*; S. Zhao,* Harvard University*; R. Jangid,* Brookhaven National Laboratory*; A. Cui,* Harvard University*; J. Sinsheimer,* Brookhaven National Laboratory*; P. Kim,* Harvard University*; N. Poccia,* IFW Dresden, Germany*; C. Mazzoli,* Brookhaven National Laboratory

Quantum computers (QC) are poised to revolutionise computational capabilities by naturally encoding complex quantum computations, thereby significantly improving computation time compared to silicon-based technologies. Currently, Q-bits, the essential components of QCs, are made from conventional superconductors that operate efficiently only near absolute zero temperatures. To address this limitation, two-dimensional van der Waals (vdW) encapsulated high-temperature superconductor (HTSC) stacks have been proposed as future Q-bit candidates, driven by recent advancements in nanofabrication techniques. However, a detailed understanding of their structural and electronic properties is crucial.

We present low-temperature resonant soft X-ray investigations on ultrathin $Bi_2Sr_2CaCu_2O_{8+y}$ (BSCCO) vdW heterostructures, promising candidates for large-scale Q-bit applications. BSCCO crystals exhibit two incommensurate lattice modulations (ILMs), providing an excellent opportunity to explore the relationship between structure and electronic behaviour in low dimensions. We report ILMs (Cu L_3) and structural peak (off resonance) maps obtained across the superconducting transition temperature ($T_c \approx 60$ K). These signals, under external gating, present significant potential for further exploration offering new insights into the electronic interactions in vdW HTSC systems.

11:00am **2D+EM+MI+QS-WeM-13 Recent Progresses in van der Waals Layered Magnetic Semiconductors***, **Young Hee Lee**,* Sungkyunkwan University, Republic of Korea **INVITED**

Ferromagnetism in van der Waals two-dimensional (2D) materials has been reported recently. Intrinsic CrI_3 and $CrGeTe_3$ semiconductors reveal ferromagnetism but the Tc is still low below 60K. In contrast, monolayer VSe_2 is ferromagnetic metal with Tc above room temperature but incapable of controlling its switching via gating due to metallic nature. Moreover, the long-range ferromagnetic order in diluted metal chalcogenide semiconductors has not been demonstrated at room temperature. The key research target is to realize the long-range order ferromagnetism, Tc over room temperature, and semiconductor with gate tunability. In this talk, we introduce magnetic dopant, vanadium in semiconducting WSe_2 and manifest Tc at room temperature and gate tunability at low doping concentration. We further explore different doping concentrations including highly degenerate regime and demonstrate unconventional magnetic order by random telegraph spin noises via interlayer coupling and more recent progresses.

Keywords: Diluted magnetic semiconductor, ferromagnetism, long-range magnetic order, Curie temperature, gate-tunability

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11:30am **2D+EM+MI+QS-WeM-15 Writing and Detecting Topological Spin Textures in Exfoliated Fe_5-xGete$_2$***, **Luis Balicas**,* Florida State University - National High Magnetic Field Lab - FSU Quantum Initiative

$Fe_{5-x}GeTe_2$ is a centrosymmetric, layered van der Waals (vdW) ferromagnet that displays Curie temperatures T_c (270-330 K) that are within the useful range for spintronic applications. Little is known about the interplay between its topological spin textures (e.g., merons, skyrmions) with technologically relevant transport properties such as the topological Hall effect (THE), or topological thermal transport. We found via high-resolution Lorentz transmission electron microscopy that merons and anti-meron pairs coexist with Néel skyrmions in $Fe_{5-x}GeTe_2$ over a wide range of temperatures and probe their effects on thermal and electrical transport [1]. It turns out that we detect a THE, even at room *T*, that senses merons at higher *T*'s as well as their coexistence with skyrmions as *T* is lowered, indicating an on-demand thermally driven formation of either type of spin texture.Remarkably, we also observe an unconventional THE, i.e., in absence of Lorentz force, and attribute it to the interaction between charge carriers and magnetic field-induced chiral spin textures. We find that both the anomalous Hall effect (AHE) and THE can be amplified considerably by just adjusting the thickness of exfoliated $Fe_{5-x}GeTe_2$, with the THE becoming observable even under zero magnetic field due to a field-induced unbalance in topological charges [2]. Using a complementary suite of techniques, including electronic transport, Lorentz transmission electron microscopy, and micromagnetic simulations, we reveal the emergence of substantial coercive fields upon exfoliation, which are absent in the bulk, implying thickness-dependent magnetic interactions that affect the topological spin textures (TSTs). We detected a 'magic' thickness of t ~30 nm where the formation of TSTs is maximized, inducing large magnitudes for the topological charge density, and the concomitant AHE and THE resistivities at T ~ 120 K. Their values are observed to be higher than those found in magnetic topological insulators and, so far, the largest reported for 2D magnets. The hitherto unobserved THE under zero magnetic field could provide a platform for the writing and electrical detection of TSTs aiming at energy-efficient devices based on vdW ferromagnets.

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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$_2$O$_5$ with plasma processes. In fsLP, crystallization is initiated as a result of non-equilibrium excited-state dynamics in the film occurring on sub-ps timescales. This produces a combination of athermal and thermal annealing expected to promote the formation of c-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_2O_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_2O_3 films were deposited at 300 °C using TMA and H_2O 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 $Pca2_1$ 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_{-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-$_2$ 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.

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} $\Omega\text{-m}^2$ 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.

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

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 13$kWcm^{-2}$ 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 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.

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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.

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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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2D Materials

Room 122 - Session 2D+EM+QS-ThA

2D Materials: Applications

Moderators: Matthias Batzill, University of South Florida, **Fei Yao**, University at Buffalo

2:15pm **2D+EM+QS-ThA-1 Tuning Functionality: Graphene Oxide (GO)/Few Layers Graphene (FLG) Membranes for Water Treatments***, J. Flores-Arciniega, S. Acosta, H. Ojeda-Galván,* CICSaB, Universidad Autónoma de San Luis Potosí, Mexico*; B. Yáñez-Soto,* Instituto de Física, Universidad Autónoma de San Luis Potosí, Mexico*; **Mildred Quintana**,* Facultad de Ciencias, CICSaB, Universidad Autónoma de San Luis Potosí, Mexico

Graphehe oxide (GO) and few layer graphene (FLG) are exciting platforms with a huge potential for developing new advanced technologies. The unique combination of properties, such as high specific surface area, charge transport, chemical stability, mechanical strength, flexibility, high electrical and thermal conductivity, make them the ideal substrates for several applications in water remediation. Here, I will describe the synthesis and processing of GO and FLG, their characterization, handling, and performance towards advanced membranes for water treatments. In particular, we aim to address the production of van der Waals heterostructures for the development of micro and nanofiltration membranes for bacteria removal, organic molecule adsorbents, and desalination. The properties of 2D materials modulate mechanical and chemical stabilities, while active sites are created by the effective construction of van der Waals heterostructures allowing charge and mass transfer producing cost-effective and highly efficient membranes for water purification.

Acknowledgments

CONAHCYT basic science project CB-A1S-8817 and Sinergía-UNAM 1564464, JF thanks to CONAHCYT for Ph.D. scholarship No. 744836. The authors want to thank Laboratorio Nacional de Ingeniería de la Materia Fuera de Equilibrio (LANIMFE), for the use of equipment and technical support.

2:30pm **2D+EM+QS-ThA-2 New Graphene Oxide-based Nanozymes for Cancer Theranostics***, A. Foti, S. Sciacca, G. Tranchida, S. Petralia, R. Fiorenza, S. Scirè, L. D'Urso, C. Bonaccorso, A. Fraix,* University of Catania, Catania, Italy*; A. De Bonis,* University of Basilicata, Italy*; **Cristina Satriano**,* University of Catania, Catania, Italy

Graphene oxide (GO) and plasmonic nanoparticles (Pd, Au, Ag NP) nanocomposites were scrutinized in this study as combinative multimodal platform with enzyme-like, photocatalytic and photothermal properties. A green one-pot chemical reduction method by using D-glucose as reducing agent and polyvinylpyrrolidone (PVP) as capping agent, was used to fabricate the hybrid 2D platforms (NP@G) and the reference plasmonic nanoparticles alone. Different molar ratios of the metal precursor/reducing agent were tested to get the best results in terms of stability, reproducibility and reaction yield, as monitored by the plasmonic band of the NPs. The physicochemical characterization of the morphological, compositional, structural, and functional properties of NP@G nanozymes was carried out in terms of X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), transmission electron microscopy (TEM), UV-visible, Raman spectroscopy, Fourier Transformed Infrared Spectrocopy (FTIR), thermocamera, atomic force microscopy (AFM), dynamic light scattering (DLS) and zeta potential (ZP). The enzyme-like activity was tested by colorimetric assays in a cell-free environment to confirm the maintenance of the nanozymes capability in the NP@G samples.The photocatalytic properties were tested in the H_2 evolution by water splitting reaction under simulated solar light. Further, the nanoplatforms were tested in prostate cancer cells (PC-3 line) in terms of cytotoxicity, cell migration and reactive oxygen species (ROS) production, to prove the antitumoral action of the developed nanomedicine. Cell imaging by laser scanning confocal microscopy (LSM) demonstrated the theranostic capability of the developed platforms, including dynamic processes at the level of sub-cellular compartments.

Acknowledgements: ADB and CS acknowledge the financial supported by MUR in the framework of PRIN2022-PNRR call under project CoMu4CaT.

2:45pm **2D+EM+QS-ThA-3 Graphene and Copper Nanoparticles Based Electrochemical Sensors for the Detection of Glyphosate in Water***, **Uswah Yasin**, F. Torrisi,* University of Catania, Italy

Glyphosate is commonly used as a herbicide to control weeds in agricultural and non-agricultural applications (Carretta, et al. J. Chromatography. A 1600, 2019), resulting in significant adverse impacts on the environment, especially contaminated soil and water, with potential effects on human health (Richmond, AESS 8, 2018). Such environmental threat recently triggered the development of enhanced and scalable glyphosate sensing technologies.

Commercial sensors for glyphosate based on gold nanoparticles (AuNPs), silver nanoparticles (AgNPs), quantum dots, show a sensitivity ranging from 0.88 μM to few pM (Zúñiga, et al. Water 14, 15, 2022). Graphene is an excellent material for sensing applications (Fenech-Salerno, et al. Nanoscale 15, 7, 2023) (Schedin, et al. Nat. Mater 6, 9, 2007). Due to the high mobility, large surface area, high mechanical strength, and chemical stability, graphene provides a versatile platform for the detection of a wide range of analytes, including glyphosate. For the detection of glyphosate, graphene-based sensors can achieve a high sensitivity of the order of 0.30×10^{-12} M (Gonçalves, et al. Mater. Today Commun. 36, 2023). In addition, graphene inks enable a large range of printed, sustainable and flexible devices (Carey, et al. Nat. Commun. 8,1, 2017).

Here, we present the preparation of a glyphosate sensor based on graphene and Cu nanoparticles, deposited by a scalable spray-coating process on flexible substrate, such as polyimide (PI) and polyethylene terephthalate (PET). The graphene ink is prepared by liquid phase exfoliation, reaching a graphene concentration of ~ 0.7 mg/ml. The spray-coated graphene ink resulted in electrodes with a sheet resistance of ~ 240 Ω/☐, subsequently spray coated with Cu nanoparticles synthesized using Pulsed Laser Ablation in Liquid (PLAL), with the concentration of 12.5 μg/ml, to form the Graphene/Cu nanoparticle (G:Cu) electrode.

The concentration of glyphosate was determined by Multiple Cyclic Voltammetry (CV) using the G:Cu electrode as the working electrode in a glass electrochemical cell loaded with a solution of glyphosate was prepared in Milli-Q water. The CV curve of G:Cu showed the presence of a redox reaction related to the oxidation states of copper ($Cu \rightarrow Cu^{2+}$), compared to a plain graphene electrode, thereby affirming the sensing efficacy of the glyphosate sensor.

Our G:Cu sprayed sensor offers a flexible, sustainable, and scalable solution to detect glyphosate with excellent selectivity and sensitivity making it the perfect approach to address the need for accurate and efficient monitoring of glyphosate contamination in environmental and agricultural settings.

3:00pm **2D+EM+QS-ThA-4 Engineering Novel Hybrid Membranes for Battery Separators from Sustainable Sources***, **Suvash Ghimire**, P. Makkar, M. Islam, K. Mukhopadhyay,* University of Central Florida

The surge in device use in transportation, biomedical sectors, and other industries is escalating at an alarming rate, coupled with grave concerns about pollution and global warming that underscores the urgency for developing efficient, safe, and environmentally friendly energy storage devices. There is a growing urgency to reduce planet-warming pollution through mining and other activities at the federal level to drop carbon emissions by half this decade and reach close to zero by the middle of the century to prevent some of the most devastating effects of climate change. Research groups worldwide are developing metal-based substitutes that address sustainability by eliminating the use and generation of hazardous substances during the synthesis and developing cheap, recyclable substitutes for electrode materials, electrolytes, membranes, and separators that are the pivotal components of energy storage devices.

Materials and their interfaces play an essential role in energy storage devices by facilitating ion transports and impeding short circuits by separating anode and cathode. Ion exchange membranes have broad applications in water electrolysis, fuel cells, and flow batteries. To date, Nafion® membranes and polyolefin-based separators are considered the industrial standards due to their excellent proton conductivity and high chemical stability. However, high cost, poor strength, shrinkage at high temperatures, and use of fluorinated chemicals hinder their widespread use. Therefore, there is an urgent need to develop membranes that can be alternatives to existing membranes without compromising the cost and environmental impact. Leveraging their porosity, properties, low cost, and thermal and chemical stabilities, clay-based membranes could be a new alternative for new-generation materials for such applications.

Our research presents a novel pathway for developing flexible and durable hybrid clay membranes by modifying them with zwitterions. The ionic conductivity of the membranes, measured using electrochemical impendence spectroscopy in a non-aqueous electrolyte solution, was found to be in the range of 10^{-4} S/cm, which is comparable to the ionic conductivities of related membranes used in electrochemical energy storage devices; this is a significant new development considering clays are insulators. Our study exhibits a new avenue to engineer highly efficient ion-conducting membranes with high thermal stability (300 °C) that can provide an efficient and recycle-free approach to developing a new generation of separators from sustainable sources for energy applications, especially for battery technology.

3:15pm **2D+EM+QS-ThA-5 Unveiling Composition-Structure Relationships for the Discovery of Novel High-Entropy 2D Materials Using the Mixed Enthalpy-Entropy Descriptor***, **Dibyendu Dey,*** University of Central Florida*; O. Ogunbiyi,* University of Missouri*; B. Ball,* University of Central Florida*; L. Liang, M. Zachman,* Oak Ridge National Laboratory*; Y. Yang,* University of Missouri*; L. Yu,* University of Central Florida

High-entropy two-dimensional materials (HE-2DMs) represent an emerging class of materials that show promise for numerous functional applications. These materials inherit the distinctive features of conventional 2D materials, such as reduced dimensionality, exceptional flexibility, and a large surface-to-volume ratio, while introducing a high configurational entropy of mixing to the system. Despite their immense potential, the experimental realm of HE-2DMs has thus far been limited to a few materials, leaving the complex interplay between their composition, structure, and synthesizability largely unexplored. In this work, by utilizing the Mixed Enthalpy Entropy Descriptor (MEED) [**1**], the material space of high-entropy 2D chalcogenides, including Group IV (Ti, Zr, Hf), Group V (V, Nb, Ta), and Group VI (Cr, Mo, W) metals in their 2H, 1T, and 1T' phases, has been systematically explored. MEED uniquely encapsulates the chemical and structural attributes critical for synthesizing HE-2DMs in their diverse polymorphs, demonstrating capabilities beyond any existing descriptor. Guided by MEED predictions, several top-candidate high-entropy tellurides and selenides, which exhibit extraordinary potential for applications in flexible electronic devices and advanced batteries, have been synthesized.

Acknowledgments: This work is supported by the US Department of Energy (DOE) Basic Energy Sciences (BES) under Award Number DE-SC0021127.

Reference:

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3:30pm **2D+EM+QS-ThA-6 Antenna-Coupled Magic-Angle-Twist-Graphene Josephson Junction Millimeter Wave Detector***, **David Castro,*** University of Central Florida

We designed a sensitive detector of THz and mm waves using an antenna-coupled magic-angle-twist-graphene Josephson junctions. Magic angle twisted bilayer graphene superconducts at a transition temperature of ~2K. We can create a lateral Josephson junction by selectively gating different sections of a single sheet of magic angle graphene. The detection mechanism in our design is based on the change in maximum zero-voltage DC current in response to an applied AC signal at the junction. We expect it to be faster than bolometric detection mechanisms while maintaining high sensitivity. We determined that the bowtie antenna would work best for this device by using finite element electrodynamic simulations. We estimated the responsivity, noise-equivalent-power, and the prospects for single-photon detection. This detector device can be used in the future for sensing applications and quantum information systems.

Acknowledgments

This work was supported by U. S. Army OSD Phase II STTR contract W911NF23C0027 and bymatching funds from the Florida High Technology Corridor (I-4) Program.

3:45pm **2D+EM+QS-ThA-7 Antenna-Coupled Graphene Josephson Junction THz/mm-wave Detector***, **Rachid Ben Khallouq,*** University of Central Florida

We will discuss design, manufacturing processes, response characteristics, and tolerance to twist-angle variations of antenna-coupled Josephson-junction detectors fabricated from magic angle graphene tailored for detecting mm-wave and THz radiation. We find that Josephson junctions realized in magic angle graphene exhibit exceptionally high dynamic resistance at the peak zero-voltage current. When a small microwave voltage is applied across the junction, it induces a change in the voltage-current correlation, resulting in a notable DC output voltage. External radiation can energize a suitable antenna, generating the required AC voltage across the junction. These detectors operate via a non-thermal mechanism, offering the potential for both speed and sensitivity. They display a bolometric response, with an estimated temperature coefficient of resistance of 300%/K. We will show different designs and detection mechanisms and compare them to other technologies.

This work was supported by U. S. Army OSD Phase II STTR contract W911NF23C0027 and bymatching funds from the Florida High Technology Corridor (I-4) Program.

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 ~ 17 μC cm^{-2} and an E_c ~ 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$_3$N$_4$ 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$_3$N$_4$ 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$_x$N$_y$H$_z$) 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-CH$_2$-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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Electronic Materials and Photonics
Room Central Exhibit Hall - Session EM-ThP
Electronic Materials and Photonics Poster Session

EM-ThP-1 Optimizing Amorphous Indium Gallium Zinc Oxide Thin Film for Application in Photoactive Layers*, **Anvar Tukhtaev**, J. Lee, J. Berdied, S. Kim,* Chungbuk National University, Republic of Korea

Amorphous metal oxide semiconductors are popular research targets due to their high performance and versatility, and are employed in a wide array of novel areas, including neuromorphic circuits. However due to the wide band gap of most metal oxides, their use in optoelectronics is very limited. Multiple methods for the fabrication of photodetectors with metal oxides have been considered in the literature, such as bilayer heterojunctions with photoactive materials and intentional defect formation to increase tail state density and reduce the band gap. Here, we demonstrate two approaches to improve the photoresponsive characteristics of amorphous indium gallium zinc oxide (a-IGZO)-based field-effect transistors. First, we prepare a bilayer of a thermally annealed a-IGZO and a polycrystalline PTCDI-C13 thin film, to combine the high mobility charge transfer of the metal oxide with the high photoresponse of the PTCDI-C13. The annealing temperature of the a-IGZO is optimized to achieve enhanced charge transport between the layers. Then, a gradient annealed a-IGZO thin film is prepared, in which a bottom layer of high temperature-annealed oxide film acts as the charge transport layer, which is complemented by a low temperature-annealed top layer. The higher disorder in the top layer increases the absorption of the film. The annealing temperatures are optimized to achieve highest mobility in the bottom layer and best photoresponse characteristics in the top layer. These methods demonstrate that metal oxides can be utilized in next-generation neuromorphic photodetection circuits such as on-hardware image recognition artificial intelligence applications.

Acknowledgements

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EM-ThP-2 Improvement of Al Undercut Defect in sub 20 Nm DRAM*, **DONG-SIK PARK**, b. Choi,* Sungkyunkwan University (SKKU), Republic of Korea

In the era of the Fourth Industrial Revolution, the utilization of high-performance and high-speed DRAM is increasingly expanding. In response to this trend, the integration density of DRAM is also improving. Since transitioning to the 10 nm design rule, scaling is continuously demanded not only for the DRAM cell size but also for the wiring. The wiring, responsible for supplying electrical signals and power to the DRAM, consists of 4 to 5 layers, with the final wiring utilizing Al lines. Low resistance is necessary to accommodate the delivery of high power for the Al layers.

The composition of Al wiring is as follows: Ti is applied as a barrier metal to connect with the Via tungsten, followed by the formation of Al wiring with a thickness of over 500 nm using the PVD method. On top of this, TiN is applied as an anti-reflecting layer. The Al wiring is patterned using lithography and dry etching techniques. With the scaling of Al wiring, the spacing between metal lines has decreased to 50 nm or less. This means that the space for dry etching the 500 nm-thick Al has become 50 nm, resulting in an aspect ratio of 10:1, posing extreme difficulty. This has led to various serious defects, with the most common being Al undercut defects.

The defect occurs when etching extends from the bottom of the Al layer to the sidewalls, causing it to disconnect. The cause of this issue is that as the aspect ratio increases, the polymer, which serves to protect the Al sidewalls during dry etching, cannot effectively reach the bottommost part, resulting in etching. To overcome this, if the shape of the Al line is formed with a positive slope, it becomes highly susceptible to Al bridge defects.

Two methods were devised to overcome this, implemented in Samsung's 20 nm DRAM technology to confirm their effectiveness. Firstly, it was observed that Al undercut defects primarily concentrated at the edges of wafer. This is influenced by the temperature of the high chuck during dry etching, and it was found that precise temperature control was difficult with the current structure. Therefore, the chuck structure was modified from 2 zones to 4 zones to enable fine temperature adjustment, and the edge area was dry etched at a lower temperature to facilitate the transmission of more polymer.Secondly, the layout structure of the Al layer was reinforced. It was found that having discontinuous vulnerable patterns was more advantageous than continuously existing patterns. Therefore, irregular step patterns were created compared to patterns resembling hammers, and their effectiveness was confirmed.These two improvements were validated through test results of real 8G DDR4 products.

EM-ThP-3 Enhancing Electro-Physical Properties of DRAM Through Control of Silicon Diffusion in Titanium Nitride Based Barrier Layer*, **Jina Kim**, Y. Kim,* Sungkyunkwan University, Korea

As DRAM cell sizes substantially scale down, silicon voids in CMOS gate electrode and memory cell bit-line connection nodes cause serious issues in DRAM performance. These voids are formed at the silicon-metal interface as a result of the each material’s difference in diffusivity, where silicon atoms are sucked into the metal layer by the Kirkendall effect, and they are accelerated by heat. Due to the increase in the heat budget of subsequent processes to over 1000 degrees, innovative process for barrier metals preventing silicon diffusion becomes critically essential. In this study, we demonstrate the impact of silicon void defects through variations in thickness, composition, and other parameters of the Titanium silicon nitride (TSN) based barrier metal. To meet the higher barrier properties, TSN has been developed as multi-layer film structure of TiN/SiN, providing low resistance even at low thickness and with the ability to control the composition of Ti, Si and N to maximize barrier properties. Increasing the thickness of TSN can increase the diffusion path of Si, thereby reducing the frequency of Si void occurrence. Furthermore, by increasing the concentration of Si within TSN, it is possible to suppress TiN grain growth while promoting amorphization or the formation of fine grains, thereby inhibiting diffusion through grain boundary. We investigated the frequency of Silicon void occurrence before and after heat treatment using SEM/TEM, and confirmed the extent of improvements for each conditions. Finally, we have confirmed improvements in DRAM data write performance as resistance and short circuit decreased due to silicon void defects. Hereby we have provided a significant opportunity for the development of 10-nano-class DRAM.

EM-ThP-4 Integrating Molecular Photoswitch Memory with Nanoscale Optoelectronics*, **Nelia Zaiats**, T. Kjellberg Jensen,* Lund University, Sweden

Using light for interconnectivity in artificial neural networks can be highly energy efficient and allow multiplexing. Important is the introduction of dynamic memory weights in these connections that can be integrated on-chip with nanophotonic components. We show that photochromic dyes, that reversibly switch their absorption of light, can be used as optical memories combined with highly efficient III-V nano-optoelectronics. We find that the dyes can be used for both short- and long-term memory by varying chemical and physical parameters of the sample, allowing to access a wide range of timescales. We demonstrate the effect both on individual nanostructures and arrays. We demonstrate the robustness over many switching cycles. Using the dye performance parameters, we find that it can function as the memory component in an anatomically verified model of the insect brain navigation complex. The work opens for artificial neural networks with energy-efficient light communication and on-chip molecular memory elements.

EM-ThP-5 Charge Trapping in a-Si_3N_4: Hydrogen as Savior and Saboteur*, **Lukas Hückmann**, J. Cottom, J. Meyer,* Leiden University, The Netherlands

Amorphous silicon nitride (a-Si_3N_4) is an essential material for nanoelectronics due to its ability to trap charges, particularly in flash memory devices. EPR experiments combined with electronic structure calculations suggest that undercoordinated Si atoms (K-centers) are responsible for this phenomenon [1]. The propensity of such defects towards hydrogen passivation, however, raises the question of the completeness of this picture.

In this work, we combine simulations at force field (FF) up to hybrid density functional theory (DFT) level. Employing the MG2 force field [2], a comprehensive statistical ensemble of structural models for a-Si_3N_4 was generated through the melt-quench procedure, ensuring robust statistical significance in our analysis [3]. Adding charges to those models, we perform structural optimization using the HSE06 hybrid DFT-functional to ensure the localization of the band edges and defect trapping energies are well described. We identify a hitherto unknown mode of intrinsic polaronic trapping of electrons in a-Si$_3$N$_4$: Charging can generate either a K-center or Si-Si-type defect. At the same time, discharging recovers the amorphous network's original structure [3]. Crucially, this study bridges the previously fragmented understanding of charge trapping and hydrogen incorporation. We demonstrate that hydrogen plays a dual role: It can repair coordination defects, healing the network, yet also promotes Si-N bond breaking in strained areas, thus compromising the network integrity [4]. Our findings offer a unified perspective on the interplay between defect formation, hydrogen behavior, and charge trapping, providing insights critical for optimizing a-Si$_3$N$_4$'s electronic properties in nanoelectronic applications.

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EM-ThP-6 Graded CdSexTe1-X /CdTe Thin-Film Solar Cells: In-Situ Dopant Profiling During Light Soaking*, **Sanghyun Lee,*** University of Kentucky*; K. Price,* Morehead State University

Cadmium Telluride (CdTe) thin-film solar cells have made significant progress in efficiency, with laboratory-scale tests surpassing 22.1%, edging closer to the theoretical Shockley-Queisser limit of around 32%. Recent research has been focused to integrate selenium (Se) into CdTe absorbers, creating band grading without CdS window layers. CdSe$_x$Te$_{1-x}$ is a prominent candidate to enhance the short-circuit-current (Jsc) by bandgap lowering below 1.45 eV. While CdS window layer intermixing mitigates the lattice mismatch, it concurrently limits absorbing light in the critical 300 - 525 nm range, resulting in efficiency loss. Thus, strategies to overcome this drawback have been focused on introducing Se to create band grading. CdSe$_x$Te$_{1-x}$ is promising, with bandgap lowering below 1.45 eV, pushing Jsc to their theoretical limit.

In this contribution, CdSe$_x$Te$_{1-x}$/CdTe devices were fabricated by vapor transport technology, and the mechanism of efficiency improvement was studied through in-situ Cu dopant profiling during light soaking. Moreover, devices were stressed at elevated temperatures simultaneously under various bias conditions, both with illumination and in the dark. The morphological and cross-sectional structure of the graded absorber were confirmed by Scanning Electron Microscopy and Electron Dispersive Spectroscopy. During light soaking, different intensities of light and temperatures were tested to characterize devices. Concurrently, we modeled the electronic structure of characterized devices using our in-house MATLAB modeling suites, connected to the external TCAD simulators, to explain the result with material and device input parameters. The results indicate that CdSe$_x$Te$_{1-x}$/CdTe devices have shallow donor and acceptor energy states near the main front junction interface. The concentration of Cu dopant is approximately 4 x 10^{14} cm^3 in the wake-up condition. The Cu dopant progresses toward the front CdSe$_x$Te$_{1-x}$ /CdTe junction during in-situ measurements.Interestingly, the stability of CdSe$_x$Te$_{1-x}$ solar cells was found to be bias-dependent and device-specific during light and dark soaking. CdSe$_x$Te$_{1-x}$ /CdTe devices without Cu dopant demonstrated depletion reduction width under light and dark-biased conditions. The depletion width of CdSe$_x$Te$_{1-x}$ devices without Cu is reduced to approximately 47 % under applied soaking conditions. Simultaneously, efficiency, Voc, and FF decreased, whereas Jsc show no clear dependency. Under light soaking conditions at 95 C, the increases in Voc, FF, and efficiency depend on light soaking conditions. The peak efficiency after 9 hr light soaking at 95 C is 12.90 %.

EM-ThP-7 Optimization of NiO Doping, Thickness, and Extension in Kv-Class NiO/Ga2O3 Vertical Rectifiers*, **Chao-Ching Chiang**, J. Li, H. Wan, F. Ren, S. Pearton,* University of Florida

We conducted a thorough analysis of vertical geometry NiO/Ga$_2$O$_3$ rectifiers using the Silvaco TCAD simulator to establish optimized breakdown voltages ranging from 1 to 7 kV. By manipulating key NiO parameters such as doping concentration (ranging from 10^{17} to 10^{19} cm^{-3}), thickness (ranging from 10 to 70 nm), and junction extension beyond the anode to form a guard ring (ranging from 0 to 30 μm), we determined the electric field distribution within each design. The factors of doping concentration, thickness, and junction extension were found to significantly influence the site of device breakdown, which could occur anywhere from the edge of the NiO extension to the edge of the top contact, consistent with experimental results. Further investigations also revealed varying breakdown voltages based on theoretical critical electric fields for different NiO bilayer thicknesses and doping concentrations.

EM-ThP-8 Theoretical Study of van der Waals Epitaxy of Bilayer Silicene on Iii-Sb Substrates*, **Kumar Vishal**, H. Huang, Y. Zhuang,* Wright State University

Research development of integrated silicon photonics in the mid-infrared (MIR) range has gained considerable momentum over the past decades, driven by its vital applications in biochemical sensing, medicine, and even astronomy communications. However, progress has been hampered by the limitation by the energy bandgap and optical transparency in conventional material. Very recently, it has been reported that 2D bilayer silicon (BLSi) demonstrates unique optical properties across the MIR spectrum. By adjusting the strain, the optical absorptions can be tuned in a wide range of wavelength from 1.5 -11.5 mm. However, experimentally the maximum in-plane strain achieved is ~7% in a lattice-matching expitaxial silicon. Remote- and Van der Waals expitaxy methods can break the lattice-mismatch constraint to obtain single crystal 2D materials, but with an insufficient in-plane strain preserved in the 2D films.

In this work, motivated by the recent achievement of dative expitaxy of single crystalline Cr5Te8 on WSe2 enduring a ~16% lattice mismatch, we conducted a theoretical study based on density function theory (DFT). Our aim is to explore the feasibility of growing BLSi on two III-Sb substrates: GaSb and AlSb. These substrates were chosen due to their ability to provide sufficient in-plane strain (11.92% and 12.23% respectively) to assure energy bandgap opening in BLSi. The generalized gradient approximation (GGA) and the strongly constrained and appropriately normed (SCAN) meta - generalized gradient approximation (meta-GGA) have been employed in the computation to analyze the chemical bond formation and to optimize the energetically favorable atomic structures. Our findings suggest that Van der Waals epitaxy of BLSi on both of the III-Sb substrates is viable when the substrate's surfaces are terminated with the metallic atoms. By forming the dative bonds between the BLSi and the III-Sb substrates, substantial in-plane strain in BLSi can be preserved, leading to a low buckled BLSi with an opened energy bandgaps.

EM-ThP-9 Low-Power, Highly Responsive Phototransistor Array Utilizing Plasma-Engineered Amorphous Metal Oxide Semiconductors*, **Uisik Jeong**, H. Rho,* Sungkyunkwan University, Korea*; S. Kim,* Sungkyunkwan University (SKKU), Republic of Korea

The potential for next-generation electronic applications is vast with the development of energy-efficient, high-performance broadband photodetectors using cost-effective amorphous metal oxide semiconductors.Commercially available photodetectors utilize various semiconductors to detect light across different wavelengths, from ultraviolet (UV) to near-infrared (NIR).However, the need for specific materials for different wavelengths limits their versatility. This study focuses on utilizing a metal oxide semiconductor, specifically indium gallium zinc oxide (IGZO), without the requirement for additional external photo absorption layers.Hydrogen (H$_2$) plasma treatment was employed to enhance charge carrier generation and create subgap states in the IGZO film, enabling wide-spectrum detection from UV to NIR without additional layers.Additionally, a ferroelectric and high-k dielectric were introduced as a gate dielectric to induce a high electric field on the channel, resulting in low-power operation.The H$_2$ plasma-treated IGZO phototransistors demonstrated ultra-high photoresponsivity (R ~ 10^3 AW^{-1}) and detectivity (D* ~ 10^{12} Jones) across abroad range of incident wavelengths (400 ~ 1000 nm), making them a promising candidate for next-generation optoelectronics.This study suggests a favorable method for the advancement of energy-efficient, cost effective, and high-performance broadband photodetectors.

EM-ThP-10 SOH Bake Time Optimization for SOH Void Reduction in Semiconductor Manufacturing*, **Jaehyeon Jeon**, B. Choi,* Sungkyunkwan University (SKKU), Republic of Korea

Spin-On Hardmask (SOH) materials are pivotal in semiconductor manufacturing for their superior masking quality, alignment accuracy, process control, and cost-effectiveness, crucial in patterning formation. However, insufficient chemical bonding between SOH and other layers, improper spin speed, or thickness can lead to void formation. In 10nm-scale DRAM products, where pattern sizes are extremely small, SOH voids can cause defects such as bridging and discontinuity in cell transistor gates. This paper demonstrates methods to minimize SOH void formation during the manufacturing process, focusing on the bake time. During SOH baking, condensation reactions and thermal degradation occur, leading to outgassing. In the early stages of baking, polymer condensation is prominent, and once cross-linking is complete, outgassing due to condensation diminishes. However, as bake time increases, outgassing due to thermal degradation becomes more significant. Thus, minimizing void formation by reducing outgassing at the completion of condensation reactions can be observed, leading to improvements in defects such as bridging and discontinuity caused by SOH voids in final patterns.

EM-ThP-11 Synthesis of Lead free $KNbO_3$ Piezoelectric Film on $LiNbO_3$ Single Crystal by Hydrothermal Method*, **Thithi Lay**, A. Hagiwara, R. Arai,* Josai University, Japan

Piezoelectric materials are in focus for many sensing applications such as vibrational sensors, pressure sensors, medical devices, wearable devices, energy harvesting devices, etc., [1-2]. Especially small scales energy harvester with clean energy sources is in demand for various portable electronics devices. Currently, the most widely used material for piezoelectric sensors is PZT because it has high piezoelectric properties compare to other. However, due to its Curie temperature the operating temperature of PZT is limited to 260℃ [5] and growing awareness of environmental hazard, lead free high temperature piezoelectric materials have been focus for new type of piezoelectric sensor [3]. To overcome with PZT in its piezoelectric properties, research and technology development are still in need and $KNbO_3$, $LiNbO_3$ and $LiTaO_3$ materials are consider as prominent candidates for lead free new and current device applications. Among them potassium niobate ($KNbO_3$) which has perovskite structure and curie temperature around 450℃ is receiving renewed interests because it has been found to exhibit high electromechanical coupling.

In this study well-ordered $KNbO_3$film were synthesis on $LiNbO_3$ single crystal substrate for the first time by hydrothermal method. Hydrothermal method has advantages in obtaining well-ordered thick film due to its reaction temperature which is possible under Curie temperature which is rather low compared to other method such as so-gel or aerosol deposition (AD) method. Crystal structure and film thickness were analyzed by SEM and XRD. $KNbO_3$ (100) and (111) structure epitaxially grown on $LiNbO_3$ (100) substrate. Grains size ranging from 1-7µm, and film thickness varies in 3-10µm. Experimental results with different reaction time showed that film thickness and grain size can be controlled by optimization of chemical reaction time in a single deposition process.

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EM-ThP-12 Thin Film Electrets Fabricated by Initiated Chemical Vapor Deposition (iCVD)*, **Stefan Schröder**, T. Hartig, L. Schwäke, T. Strunskus, F. Faupel,* Kiel University, Germany

Electrets are the electrostatic counterpart to permanent magnets, as they provide a (quasi-)permanent electric field. They have attracted great interest in the field of electronic applications ranging from sensors to energy harvesting. Polymers are usually selected as the starting material for the fabrication of stable electrets. New application pathways, e.g. in organic electronics, are increasing the demand for such materials in the form of thin films. Current wet-chemical polymer thin film fabrication is limited in the production of precise electret film thickness and dielectric breakdown strength. The reason for this are surface tension and dewetting effects in solution-based approaches as well as residual solvent molecules. This work highlights the fabrication of ultra-stable electret films by vapor phase deposition. Solvent-free, single-step initiated chemical vapor deposition (iCVD) is applied to fabricate precise polymer thin films of high dielectric breakdown strength on large-area substrates as well as complex geometries. Suitable material compositions are identified with the help of first principle calculations, based on electronic structure calculations. Furthermore, polarization effects are investigated, which result in long-term stability and precise tailoring of the iCVD electret surface potential. The fabricated films are tested in different electret transducers and show great potential for the application in next-generation devices.

EM-ThP-13 Interfacial Triangular Nanostructure Formation During Annealing of GaAsSb on InP*, **Leonid Miroshnik**, D. Shima,* University of New Mexico*; A. Li,* University of Pennsylvania*; G. Balakrishnan,* University of New Mexico*; T. Sinno,* University of Pennsylvania*; S. Han,* University of New Mexico

Antimonide-based semiconductors (e.g., GaSb, InSb, AlSb) and their ternary/quaternary alloys are essential for high-operating temperature infrared devices, including thermal and photoelectric detectors, due to their narrow bandgaps which span the entire mid-wave infrared spectrum. However, the low melting points and chemical degradation modes of antimonide III-V materials pose significant manufacturing challenges when fabricating subsequent devices. In this work, we anneal epitaxial lattice-matched GaAsSb films grown on InP and capped with PECVD silicon nitride to show that atomic species rapidly diffuse across the heterojunction at temperatures as low as 675 °C. XRD and Raman analysis suggest the presence of Sb-rich and As-rich structures. Using TEM-EDX and geometric phase analysis, we show that antimony and indium diffuse across the epitaxial interface and create triangular structures composed of GaP faces with an InSb perimeter. The triangles range in height from 20 to 700 nm with an average height of 50 nm. Crystalline InSb nanostructures are observed at the tips of the triangles. These structures provide an opportunity for engineering the interface of antimony-based semiconductors and a potential method for the formation of confined InSb quantum structures. Furthermore, we discuss a mechanism in which this degradation mode may be enhanced or mitigated through film-strain engineering.

EM-ThP-14 Metal Matrix Composite Metallization Improves PV Module Efficiency and Electrical Bridging of Solar Cell Cracks for Durability*, A. Chavez,* University of New Mexico*; A. Jeffries,* Osazda Energy*; **Sang Han**,* University of New Mexico*; S. Huneycutt, A. Ebong,* University of North Carolina at Charlotte*; D. Harwood, N. Azpiroz,* D2Solar*; B. White, B. Boyce,* Sandia National Laboratories

We have optimized the material properties of screen-printed, silver-carbon-nanotube-composite electrical contacts on Passivated Emitter and Rear Contact cells. We demonstrate that optimized carbon-nanotube-reinforced composite metallization increases ductility, fracture strength, and electrical cell-crack-bridging characteristics of gridlines over the conventional silver metallization. The fracture patterns, observed under *in situ* scanning electron microscope tensile tests, reveal that the increased ductility gives rise to much more pronounced slant fracture with an elongated metal overhang than the standard metallization. Finite element modeling is used to corroborate this observation. We visualize the plane stress condition near the crack tip, where the breakdown in triaxiality of stress leads to the slant fracture pattern. Tension test on individual gridlines, exfoliated from the substrate, further illustrates an increase in fracture toughness by a factor greater than 7x for the composite metallization, being consistent with the observation of pronounced overhang from the fractured gridlines. The improved ductility and fracture toughness ultimately result in electrical bridging of cell cracks wider than 65 µm. The composite metallization additionally provides a statistical increase in cell efficiency by 0.03%, full-sized module efficiency by 0.1%, and maximum power point by 1%, likely due to enhanced sintering of silver particles within the composite paste. We anticipate that our approach is easily translational to copper and aluminum pastes as well as recent cell technologies such as Tunnel Oxide Passivated Contact cells.

EM-ThP-15 Revisiting Materials from the B-C-N Family for Interconnect Dielectric Applications*, **Michelle Paquette**, R. Bale, F. Berber Halmen, G. Bhattarai, S. Daneshmehr, S. Dhungana, M. Stoll,* University of Missouri-Kansas City

Fundamentally, the back-end interconnect system is made up of two material types: a metallic conductor, and an insulating dielectric. With the ongoing push for high-performance computing, the higher device and power density as well as speed requirements for integrated circuits place new and more challenging demands on these materials. As the semiconductor industry perseveres toward a replacement for the copper conductor, multiple different challenges face dielectrics, including more stringent deposition control, patterning flexibility, and property specifications (electrical, mechanical, thermal, etc). Boron-based solids have been considered as an alternative to silicon-based dielectrics due to their combination of potentially ultra-low dielectric constant with robust mechanical, electrical, and chemical properties. This contribution will cover recent advances and future potential for boron-based dielectrics from our group and others.

EM-ThP-16 Photoluminescence Measurements of Te-Doped Gasb from 10 K to 300 K Using FTIR Spectroscopy, *S. Yadav, **Sonam Yadav**, C. A. Armenta, J. R. Love,* New Mexico State University*; P. C. Grant,* University of Arkansas*; S. Zollner,* New Mexico State University

Gallium antimonide (GaSb) is a vital semiconductor for fabricating infrared optoelectronic devices, making it significant for next-generation infrared imaging systems. In this study, we investigated the photoluminescence (PL) properties of Te-doped GaSb with a doping level of 2 – 5 x 10^{17} cm^{-3}, across a temperature range from 10 K to 300 K using 400 mW laser power by using Fourier Transform Infrared Spectroscopy (FTIR) in the near IR spectral range. Our experimental results revealed that at room temperature, GaSb exhibits weak PL, which significantly increases as the temperature drops below 170 K. At 10 K, the PL intensity peaks sharply, corresponding to the direct band gap of 0.726 eV. As the temperature increases to 170 K, an additional peak emerges around 0.75 eV, which we attribute to the indirect recombination of L-valley electrons. We quantified the total number of electrons in both the L and Γ valleys, and the ratio of those enabling us to calculate the carrier concentration in each valley as a function of temperature. Our interest in GaSb PL stems from its analogous behavior to GeSn alloys with 10% Sn, making it a potential candidate for use in photodetectors. This work provides valuable insights into the temperature-dependent electronic properties of GaSb, highlighting its relevance in advanced optoelectronic applications.

EM-ThP-17 Atomic-Level Insights into RRAMs: Improving Performance and Energy Efficiency for Advanced Computing, *M. Chowdhury, A. Moazzeni, **Gozde Tutuncuoglu,*** Wayne State University

Conventional von-Neumann computing systems face significant limitations due to the memory-processor bottleneck, which restricts simultaneous data retrieval and instruction execution, leading to increased energy consumption and reduced performance. To surpass this bottleneck, next-generation computing devices must achieve substantial improvements in processing speed and energy efficiency. Emerging non-volatile memory technologies, such as resistive random access memories (RRAMs) based on crossbar arrays, offer a promising solution by integrating memory and computation, thereby enhancing computational efficiency and reducing energy usage.

In this talk, we will explore the resistive switching dynamics of non-volatile RRAM by analyzing their atomic and electronic structures. Our focus will be on transition metal oxide RRAMs fabricated using DC-sputtering and Atomic Layer Deposition (ALD) techniques, known for their high performance and compatibility with CMOS technology. We aim to provide detailed insights into how materials properties, such as stoichiometry, affect device performance metrics and how these properties can be modified using data-guided experimental techniques.

Our research objectives center on capturing the intricate details of these structures to optimize the performance of RRAM devices. By leveraging atomic-level insights, we aim to tailor these devices to meet the specific requirements of various computing algorithms. This optimization will be guided by advanced device-to-algorithm benchmarking tools, facilitating a comprehensive analysis linking the atomic and electronic properties of RRAMs to their overall performance in computational applications.

Through this approach, we expect to provide materials-focused pathways to enhance the efficiency and reliability of RRAMs, thereby making them a more viable option for future in-memory computing technologies. This talk will contribute to the fundamental understanding of RRAMs and present practical solutions for optimizing their use in advanced computing systems.

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.

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.

References

1. Kurz, N. *et al.* Experimental determination of the electro-acoustic properties of thin film AlScN using surface acoustic wave resonators. *Journal of Applied Physics* **126**, 075106 (2019).

2. Akiyama, M., Umeda, K., Honda, A. & Nagase, T. Influence of scandium concentration on power generation figure of merit of scandium aluminum nitride thin films. *Applied Physics Letters* **102**, 021915 (2013).

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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.

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