Atomic Scale Processing Focus Topic
Room 317 - Session AP+2D+AS+EM+PS+SS+TF-MoM

Area Selective Processing and Patterning

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

8:20am **AP+2D+AS+EM+PS+SS+TF-MoM-1 Imperfectly Perfect Materials and/or Processes as a Route for ASD**, ***Christophe Vallee***, SUNY POLY, Albany; *M. Bonvalot, M. Jaffal, T. Yeghoyan,* University Grenoble Alpes, LTM, CNRS, France; *N. Posseme, R. Gassilloud, T. Chevolleau,* CEA/LETI-University Grenoble Alpes, France **INVITED**

In recent years, many strategies have been presented to selectively deposit a material on a specific surface (area selective deposition), or space direction (topographically selective deposition). Whatever the selective process developed to this end (inherent delay, surface inhibition, surface activation, super-cycles...), it is expected that a perfect material is perfectly deposited on the surface at stake. However, this most often implies that some imperfect material is thereby deposited on surfaces where no growth is expected. Taking this logic a little further ahead, we can even imagine that it may not be at all necessary to develop perfect ALD processes to achieve ALD-based selective deposits.

In this presentation, we will show how imperfect ALD processes can be developed by working out of the ideal precursor ALD window or regime, to adequately lead to ASD processes. We will also show that the requirements of an ideal growth inhibition of no-growth surfaces can be successfully circumvented for ASD processes. Indeed, the simultaneous deposition of a same material on two differing substrates can lead to inherent discrepancies in the materials quality, that can be advantageously taken into consideration in the development of a localized bottom-up growth strategies by adding a selective etching step.

9:00am **AP+2D+AS+EM+PS+SS+TF-MoM-3 Area Selective Deposition on EUV Photoresist**, ***Rosanna Robert***, SUNY College of Nanoscale Science and Engineering; *H. Frost, K. Lutker-Lee,* TEL Technology Center, America, LLC, USA; *C. Vallée,* SUNY College of Nanoscale Science and Engineering

Area selective deposition (ASD) is a key process required for the next generation of nanotechnology. ASD utilizes surface chemistry and reaction modifications to promote growth on one of two different materials. When applying an ASD process to a patterned wafer with both materials exposed, we can selectively grow a film on one surface while blocking growth on the other surface (known as the nongrowth area). One application for ASD is ultra-thin extreme ultraviolet (EUV) photoresist repair to enable continued pitch scaling in the Back End of Line[1]. Pattern transfer fidelity depends on initial line edge roughness (LER) and line width roughness (LWR) values of the EUV resist. Moreover, local critical dimension uniformity (LCDU) for <30 nm critical dimension hole patterning also varies with the initial resist thickness[2]. In this project, we propose to develop an ASD on EUV resists before or alternatively during an etch process to improve LCDU and LER/LWR; in this case, the ASD is used as a corrective step.

To develop an ASD process that is relevant to device manufacturing, we only consider the gases present on a plasma etch chamber as precursors for ASD. We utilize the plasma assistance of the etch chamber to develop an ASD process by Plasma enhanced chemical vapor deposition, rather than by the more commonly exploited atomic layer deposition. This is more challenging since radicals from precursor dissociation are known to be highly reactive on the surface. However, it was recently demonstrated the selective PECVD of a silicon film on SiON surfaces using SiF4/H2 plasma[3].

In this presentation, we will demonstrate ASD by PECVD on SnOx (a EUV resist material) vs SiO-based materials (underlayer) in a 300 mm plasma etch tool, and the impact of plasma precursors and parameters on selectivity. We will show that we can selectively deposit film on SnOx. Results on full wafers and patterned samples will be presented. Thanks to the use of an in-situ plasma diagnostic, such as optical emission spectroscopy, as well as of ex-situ surface diagnostics such as X-ray photoelectron spectroscopy and scanning electron microscopy, we will discuss the mechanisms inherent to the selective growth and discuss the impact of chemistry of neighboring materials and pattern density.

1 J.Church, "Plasma based ASD for EUV resist defectivity reduction and process window Improvement" *AVS* (2021) Nov 2020

2 B. Vincent et al, Proc. *SPIE 11323,* "Extreme Ultraviolet (EUV) Lithography XI,"1132326 (23 Mar 2020)

3 G. Akiki et al, "Origin of area selective plasma enhanced chemical vapor deposition of microcrystalline silicon," *J. Vac. Sci Technol.A* 39 (2021) 013201

9:20am **AP+2D+AS+EM+PS+SS+TF-MoM-4 Impact of Post-Exposure Treatments on TMSDMA-Passivated SiO_2 Surfaces**, ***Anthony Valenti***, *C. Vallée, C. Ventrice,* SUNY Polytechnic Institute, Albany; *K. Tapily, K. Yu, S. Consiglio, C. Wajda, R. Clark, G. Leusink,* TEL Technology Center, America, LLC

As the scale of semiconductor devices continues to shrink, conventional approaches to fabrication such as photolithographic patterning are becoming limited in their ability to provide the precision and resolution required for smaller and smaller features. Over the last several years, a bottom-up and self-aligned patterning technique known as area-selective deposition (ASD) has been explored. With this technique, the deposition process is manipulated in such a way as to only promote growth on one type of surface on a patterned substrate. This is typically achieved by inhibiting specific surfaces through the selective chemisorption of molecules that are inert to the reactants used for growth of the material of interest. Aminosilane precursors such as *N*-(trimethylsilyl)dimethylamine (TMSDMA) are of recent interest due to their potential use in area-selective atomic layer deposition (AS-ALD). With their strong selective chemisorption on SiO_2 surfaces versus Si and non-oxidized metal surfaces, these precursors can be used to block deposition of metals on SiO_2 while not inhibiting growth on Si or metal surfaces. For aminosilanes to be used as inhibiting precursors in AS-ALD, the resulting layer must maintain its passivation throughout a dozen or more ALD cycles. This study investigates the impact of various common ALD co-reactant/post-exposure treatments on SiO_2 surfaces passivated via exposure to TMSDMA, including ozone exposure, H_2 plasma treatment, and H_2 plasma treatment followed by H_2O vapor exposure. This project also explores using a second inhibitor dosing via NF_3 plasma treatment in order to fluorinate any nucleation sites left vacant on the SiO_2 surface after TMSDMA exposure. These treatments were conducted on samples of TMSDMA adsorbed on Si(100) substrates with 1000 Å thick thermal oxide surfaces. Water contact angle measurements were taken of each sample to determine relative surface passivation of each sample and to monitor temporal degradation of the surfaces over a timescale spanning weeks. Angle-resolved X-ray photoelectron spectroscopy and attenuated total reflection/Fourier transform infrared spectroscopy were performed in order to determine the chemical state of each surface. Temperature programmed desorption measurements were conducted to assess the relative coverage of the inhibiting film on each sample and their stability at higher temperatures.

9:40am **AP+2D+AS+EM+PS+SS+TF-MoM-5 Area-Selective ALD Using Small Molecule Inhibitors of Different Sizes: Single and Sequential Inhibitor Dosing**, ***Pengmei Yu***, *M. Merkx, I. Tezsevin,* Eindhoven University of Technology, Netherlands; *P. Lemaire, D. Hausmann,* Lam Research Corp.; *T. Sandoval,* Federico Santa María Technical University, Chile; *W. Kessels, A. Mackus,* Eindhoven University of Technology, Netherlands

Due to the continuous scaling of semiconductor device features, area-selective atomic layer deposition (ALD) is gaining attention for enabling bottom-up fabrication with atomic-scale control. Area-selective ALD can be achieved by surface deactivation of the non-growth area using inhibitor molecules. Small molecule inhibitors (SMIs) are of great interest due to the vapor-phase application and corresponding industrial compatibility.[1] Our previous work established that SMIs block precursor adsorption by a combination of chemical passivation of surface sites and steric shielding.[2] In this contribution, we compared three SMIs of different sizes for SiO_2 inhibition on the Al_2O_3 surface, namely acetic acid (HAc), acetylacetone (Hacac), and 2,2,6,6-tetramethyl-3,5-heptanedione (Hthd), and explored sequential dosing of two different SMIs to increase the overall inhibitor packing.

We first focused on the use of a single SMI and studied how the size influences their performance. By in-situ spectroscopic ellipsometry and infrared spectroscopy studies, it is observed that using either a smaller (HAc) or a larger (Hthd) SMI than Hacac[3] could improve SiO_2 ALD inhibition. Density functional theory and random sequential adsorption simulations were performed to further understand experimental findings. We found that although both steric shielding and chemical passivation are required for effective precursor blocking by SMIs, neither of them plays a dominating role. As compared to Hacac, HAc performs better due to its small size, yielding denser packing and thereby a higher degree of chemical passivation. Hthd on the other hand, benefits from its bulkiness, resulting in a higher contribution from steric shielding.

In an effort to achieve a higher selectivity, we explored whether sequentially dosing of two different SMIs can lead to higher surface coverage and deactivation. It is found that enhanced precursor blocking of 98.4 ± 0.2 % could be achieved by dosing HAc and Hthd sequentially, which is higher than either 96.0 ± 0.6 % by Hthd or 97.0 ± 0.5 %by HAc solely. Results for various combinations of inhibitors and sequences will be presented.

In summary, this work illustrates that varying the size of SMIs could bring benefits from either higher steric shielding or chemical passivation components for improved precursor blocking performance. In addition, it is demonstrated that combination of SMIs could potentially be an effective strategy for achieving higher selectivity.

[1] A.J.M. Mackus *et al.*, Chem. Mater. 31, 2 (2019).

[2] M.J.M. Merkx *et al.*, J. Phys. Chem. C 126, 4845 (2022).

[3] M.J.M. Merkx *et al.*, J. Vac. Sci. Technol. A 39, 012402 (2021).

10:00am **AP+2D+AS+EM+PS+SS+TF-MoM-6 Role of Catalytic Surface Reactions During Area-Selective Tan ALD for Precursor Blocking Using Aniline Molecules**, ***Marc Merkx***[1], *I. Tezsevin, P. Yu, R. Heinemans, R. Lengers, E. Kessels, A. Mackus,* Eindhoven University of Technology, Netherlands; *T. Sandoval,* Federico Santa Maria Technical University, Chile

The semiconductor industry is running into significant issues regarding RC-delays in state-of-the-art interconnect structures. A solution is to selectively deposit the transition metal nitride diffusion barrier on the dielectric via sidewalls but not at the bottom, known as a bottomless barrier structure.[1]. In this contribution, area-selective TaN ALD is investigated using aniline as a small molecule inhibitor (SMI),[2] with the focus on studying the catalytic surface reactions that take place on the metal non-growth area after aniline adsorption.

Area-selective TaN ALD was achieved using a three-step (i.e. ABC-type) ALD cycle using: (A) aniline as SMI, (B) tert-butylimidotris(dimethylamino)tantalum (TBTDMT) as the precursor molecule, and (C) an Ar-H_2 plasma as the co-reactant. This process was found to selectively deposit TaN on dielectric surfaces (e.g. Al_2O_3 and SiO_2) considering the metal surfaces (e.g. Co, Ru) as non-growth area. It was observed that the selectivity of the process is strongly dependent on the employed substrate temperature. At 175 °C only ~1 nm TaN can be deposited selectively, whereas by raising the substrate temperature to 300 °C ~3 nm of selective TaN growth was achieved on Al_2O_3, with respect to Ru as the non-growth area.

An explanation for the strong temperature dependence for the selectivity of this process could be the catalytic reactivity of the metal non-growth area. For example, through density functional theory (DFT) calculations, it was found that aniline can undergo a hydrogenolysis reaction on transition metal surfaces, where the amine group splits off as NH_3 while benzene remains adsorbed on the surface. This reaction eliminates the NH_2 groups from the surface that could otherwise interact with incoming precursor molecules.[3] Experimental and simulation results will be presented to provide insight into the role that catalytic surface reactions play during area-selective ALD on metal surfaces.

[1] Merkx et al., Atomic Limits **7**, (2022) https://www.atomiclimits.com/2022/04/18/

[2] Merkx et al., Chem. Matter **32**, 7788-7795 (2020)

[3] Merkx et al., Chem. Matter. **32**, 3335-3345 (2020).

10:40am **AP+2D+AS+EM+PS+SS+TF-MoM-8 AVS Russell and Sigurd Varian Awardee Talk: Sequential Application of Two Inhibitors to Achieve Area-Selective Atomic Layer Deposition of Dielectric on Metal**, ***Tzu-Ling Liu***[2][3], *M. Harake, S. Bent,* Stanford University

Area-selective atomic layer deposition (AS-ALD), which provides a bottom-up approach to fabricate patterned structures, has been considered as a prospective solution to overcome the challenges in current semiconductor manufacturing processes. To enable more applications of AS-ALD, it is critical to expand the AS-ALD toolbox to different types of surfaces. Previous studies have successfully demonstrated selective deposition of dielectrics on the dielectric (DoD) regions of metal/dielectric patterns using alkanethiols and phosphonic acids as the inhibitors for metal surfaces. However, doing the reverse pattern transfer, i.e., selective deposition of dielectrics on the metal (DoM) regions, is less well-investigated because selective inhibitor deposition on dielectric over metal is more challenging. Taking organosilane, a common inhibitor choice for dielectric surfaces, as an example, it can also adsorb on metal substrates when native metal oxide is present. Hence, it is important to develop a strategy to protect metal surfaces from the adsorption of organosilane inhibitors for achieving AS-ALD of DoM.

In this work, we demonstrate a two-step strategy to achieve selective deposition of DoM by using two different SAMs with orthogonal surface chemistry, i.e., one SAM preferentially adsorbs on the metal, which serves as a protector to prevent the adsorption of the other SAM onto the metal, and the other primarily adsorbs on the dielectric, which serves as an inhibitor for AS-ALD. We sequentially perform dodecanethiol (DDT) deposition on Cu surfaces, followed by octadecyltrimethoxysilane (OTMS) deposition on SiO_2 surfaces. Since the Cu surfaces are protected by DDT in the first step, OTMS selectively forms a well-packed self-assembled monolayer (SAM) only on SiO_2. With this strategy, we demonstrate AS-ALD of ZnO and Al_2O_3 on Cu (growth surface) over SiO_2 (non-growth surface) after applying a thermal step to selectively remove DDT protector from Cu. The blocking results show that selectivity > 0.9 can be maintained after 35 cycles of ZnO ALD (corresponding to 5.6 nm of ZnO on a reference native SiO_2-covered Si substrate) and 15 cycles of Al_2O_3 ALD (corresponding to 1.4 nm of Al_2O_3), respectively, using this sequential two-step SAM process. Our study helps expand the selective deposition toolbox and provide more possible applications for AS-ALD in next generation electronic devices.

11:00am **AP+2D+AS+EM+PS+SS+TF-MoM-9 Carborane Self-Assembled Monolayers for Area-Selective Deposition**, ***Michelle Paquette***, *R. Bale, R. Thapa, S. Pinnepalli,* University of Missouri-Kansas City; *J. Bielefeld, S. King,* Intel Corporation

Area-selective deposition (ASD) is an important strategy in improving the fidelity of and/or reducing the complexity of current multi-pattern pitch-division processes. An expanded palette of ASD materials and processes is needed. Boron carbide (BC) has been demonstrated to be a compelling candidate for low-*k* dielectric, etch stop, diffusion barrier, and patterning-assist layers, due to its robust electrical, mechanical, and chemical properties, as well as unique etch chemistry. The molecular carborane precursor is of interest for BC-based self-assembled monolayers (SAMs). This is a symmetric twelve-vertex molecule, with many available and typically sublimable derivatives. For SAM applications, carborane stands out in that its 3D symmetry allows for the formation of well-ordered layers, and the termination of its vertices by labile H atoms allows for cross-linking with a variety of mechanisms including heat, plasma, and radiation (e.g., UV, e-beam). Carborane SAMs can conceivably fulfill various roles in ASD schemes, including as an intrinsically selective functional dielectric layer (e.g., diffusion barrier), sacrificial layer (e.g., hard mask), direct-writeable layer, or blocking layer to facilitate the selective deposition of other materials. We describe progress in the deposition and characterization of carborane SAMs toward the development of a range of ASD schemes and applications.

11:20am **AP+2D+AS+EM+PS+SS+TF-MoM-10 Peter Mark Memorial Award Talk: Reactive Inhibitory Chemistries for Area Selective Depositions and Their Application in Back End of the Line Processes**, ***Rudy Wojtecki***[4], IBM Almaden Research Center **INVITED**

Area selective depositions (ASD) describe self-aligned processes where the chemical contrast of surfaces are exploited to selectively grow a film. ASD can be applied to a variety of fabrication schemes to improve tolerance to overlay errors in fully aligned via schemes or achieve device performance improvements by reduce resistance between interconnect levels in barrier-less contacts that reduce stage delay. While ASD processes are accessible through a variety of methods – differences in surface reactivities between materials, self-assembled monolayers (SAMs) and small molecule inhibitors, to name a few – reactive organic inhibitors and their application in ASD processes will be described. Reactive inhibitor compositions can be selectively deposited on a metal portion of a pre-pattern surface, then undergo (i) a crosslinking reaction or (ii) further chemical transformations used to grow an inhibitory film to a desired thickness. Crosslinking of a monolayer film for ASD was demonstrated with the introduction of diyne moieties into a SAM composition, which is crosslinked under either UV or thermal treatment. These crosslinked monolayers were found to enhance selectivity in an ASD process and reduce defects on patterned substrates.

[1] **2021 TFD James Harper Awardee**

[2] **TFD James Harper Award Finalist**

[3] **AVS Russell and Sigurd Varian Awardee**

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

With synthetic modifications to increase the length of the SAM, further reductions in defectivity was achieved as well as the ASD of TaN. Electron beam irradiation of aliphatic moieties are also known induce crosslinking. With the use of hydroxamic acid head groups the chemical contrast between exposed (crosslinked) and non-exposed regions could be significant enough to enable a patternable ASD process where, as the crosslink density increased the selectivity of the monolayer is further improved. These SAM chemistries require solution-based coating methods but the concept of a crosslinkable inhibitor could also be translated to a vapor phase process, demonstrated with propargyl amine and vinyl pyridine. To tailor inhibitor thickness in strategy (ii) chemically reactive surfaces were exploited where monomers are selectively attached to a metal surface then polymers grown in an area selective manner with tailorable thicknesses, demonstrated with a polynorbornene and poly(vinylpyridine). This tailorable thickness presents several advantages over monolayers – such as enabling ASD on patterns with topography (sharp corners & bends) or the control of lateral overgrowth. These reactive inhibitory chemistries demonstrate an inhibitory chemistry strategy for ASD and their use in back end of the line applications such as fully aligned via, barrier-less contacts or zero-line end extensions.

Nanoscale Science and Technology Division
Room 304 - Session NS3+EM+TF-MoM

Nanophotonics, Metasurfaces and Plasmonic Systems Including Inverse Design Methods

Moderators: David Czaplewski, Argonne National Laboratory, **Nikolai Klimov**, National Institute of Standards and Technology

11:20am **NS3+EM+TF-MoM-10 Quantum and Nonlinear Photonics in Silicon Carbide with Inverse Design***, **Daniil Lukin**, J. Vuckovic,* Stanford University **INVITED**

Integrated photonics technology has achieved the degree of scalability and complexity needed for building up photonic quantum computers based on optically-addressable spin qubits such as color centers. However, at present none of the industry-standard photonics materials host high quality color centers. Silicon Carbide has the potential to become a technologically-mature platform that can close this longstanding gap between classical and quantum photonics devices. I will discuss the recent progress of Silicon Carbide integrated photonics for quantum and nonlinear applications, as well as the applications of inverse-design for novel photonics functionalities.

Surface Science Division
Room 319 - Session SS+AS+TF-MoM

Dynamics and Mechanisms at Surfaces and Interfaces

Moderator: Eric Altman, Yale University

8:20am **SS+AS+TF-MoM-1 Stereodynamics Effects in Grazing-Incidence Fast-Molecule Diffraction***, **Cristina Díaz**,* Universidad Complutense de Madrid, Spain **INVITED**

Grazing-incidence fast-projectile diffraction, measured experimentally for the first time in 2007[1,2], has been proposed both as a complement and an alternative to thermal-energy projectile scattering, which explains the interest that this technique has received in recent years, especially in the case of atomic projectiles (GIFAD)[3,4]. Grazing-incidence fact-molecule diffraction (GIFMD), on the other hand, has received much less attention (mostly theoretical[5,6]), despite the fact that the H_2 molecule:(i) is as easy to generate as atomic H (a widely used projectilein GIFAD experiments); (ii) is lighter than He (another widelyused projectile in GIFAD), which would further reduce surface-phononsinelastic processes; and (iii) can reveal aspects of thesurface landscape that may be relevant in other contexts dueto the internal degrees of freedom (DOFs) and, in the case ofthe ionic surfaces, to the interaction of its quadrupole momentwith the electric field created by the ionic crystal, which is verysensitive to the surface details.Here, we present a theoretical study of grazing-incidence fast-molecule diffraction of H_2 from KCl(001) usinga six-dimensional density functional theory based potential energy surface and a time-dependentwavepacket propagation method. The analysis of the computed diffraction patterns as a function ofthe molecular alignment, and their comparison with the available experimental data, where the initialdistribution of rotational states in the molecule is not known, reveals a puzzling stereo dynamics effectof the diffracted projectiles: Diffracted molecules aligned perpendicular, or quasi perpendicular,to the surface reproduce rather well the experimental diffraction pattern, whereas those moleculealigned parallel to or titled with respect to the surface do not behave as in the experiments. Theseresults call for more detailed investigations of the molecular beam generation process.

1- P. Rousseau, et al., Phys. Rev. Lett., 98, 016104 (2007).

2- A. Schuller et al., Phys. Rev. Lett., 98, 016103 (2007).

3- H. Winter and A. Schuller, Prog. Surf. Sci., 86, 169 (2011).

4- M. Debiossac, P. Pan and P. Roncin, Phys. Chem. Chem. Phys., 23, 7615 (2021).

5- M. del Cueto et al., Phys. Chem. Chem. Phys., 19, 16317 (2017).

6- A. S. Muzas et al., Phys. Rev. B, 96, 205432 (2017).

9:00am **SS+AS+TF-MoM-3 Intermolecular Interactions in Carbonyl Compounds Trigger Surface Reactivity***, **Swetlana Schauermann**, S. Attia, C. Schroeder, M. Schmidt,* Kiel University, Germany

Hydrogenation of carbonyl compounds is an important step in many applications in heterogeneous catalysis. This class of reactions is, however, experimentally highly challenging as it requires the activation of a normally very stable C=O bond. There is an ongoing discussion on an alternative mechanism of C=O bond hydrogenation, which involves keto-enol tautomerization as a first step. In this mechanism, a H atom transfers to oxygen in an intramolecular process to produce a C-O(H) single bond, leaving behind a C=C double bond and forming the enol species. Several theoretical studies predict a significantly lower activation barrier for hydrogenation of the C=C bond in enol as compared to the direct hydrogenation of the C=O bond in ketone for different classes of mono- and dicarbonyl compounds.

In this contribution, we present a mechanistic study on atomistic-level mechanisms of enol formation and stabilization via lateral interactions with co-adsorbed surface species over catalytically active metal surfaces (Pt and Pd).[1, 2] We employ a broad range of carbonyl compounds including acetophenone, acetylpyridine, butanal and ethyl pyruvate, whose adsorption and reactivity behavior were investigated using a combination of infrared reflection absorption spectroscopy (IRAS), scanning tunneling microscopy (STM) and molecular beam techniques. We found that enols can be efficiently formed in different types of carbonyl-containing molecules, however, they require stabilization on the surface via lateral interaction, e.g. by establishing hydrogen bonding between the –OH group of an enol and a carbonyl group of the neighboring adsorbate. Stabilization of formed enols via lateral interactions with the adjustment molecules results in formation of different types of oligomers, including one of more enol molecules. The efficiency of enol formation was found to strongly depend on the chemical structure of the adsorbates and can be affected by e.g. the insertion of the functional groups, such as phenyl or pyridine groups. Also the presence of subsurface hydrogen in Pd was shown to strongly enhance keto-enol tautomerisation in some of the investigated carbonyls. Finally, we provide the first experimental evidence for a low-temperature hydrogenation pathway of carbonyl compounds, which occurs in ketone-enol dimers of acetophenone formed on Pt.[3] In this process, stabilization of enol species via lateral interactions with a neighboring carbonyl is crucial for enabling the target hydrogenation pathway.

1. Attia, S. et al *Angew. Chem. Int. Edit.* **2018,***57*, 16659.
2. Attia, S.et al *ACS Catal.* **2019,***9*, 6882.
3. Attia, S. et al, *J. Phys. Chem. C* **2019,***123* (48), 29271.

9:20am **SS+AS+TF-MoM-4 Velocity Map Images of Subsurface Oxygen Desorbing from Rh(111)***, **Arved Cedric Dorst**, T. Schäfer,* University of Göettingen, Germany*; D. Killelea,* Loyola University Chicago

In heterogeneous catalysis, the reactivity of for example oxidation reactions is often enhanced by transition group metal surfaces as catalysts. After exposure, the oxygen molecules readily dissociate into oxygen atoms on the surface forming characteristic surface reconstruction patterns. However, not only the formation of surface oxygen (O_{surf}) structures but also of subsurface oxygen (O_{sub}) phases is possible, especially when aggressive oxidation agents such as NO_2 or atomic oxygen are used as oxygen source. The O/Rh(111) has been adapted as a benchmark system for O_{sub} formation in the past. In temperature programmed desorption (TPD) experiments, O_{sub} emerges as a narrow desorption feature around 800 K, while O_{surf} forms a subsequent broad desorption feature over

several 100 K. Although extensive research has been done on the formed reconstructions of O_{surf}, few is known about the microscopic details of O_{sub} formation.

In the here presented work, velocity map imaging (VMI) was applied to the O/Rh(111) system. We combined TPD and VMI to investigate recombinatively desorbing O_{sub} from Rh(111). This allows a precise assignment of high-resolution velocity distributions of desorption products to certain TPD peaks. We observe a hyperthermal velocity distribution for recombinatively desorbing oxygen from subsurface as well as from surface states. These results provide valuable benchmark data, on which theoretical models describing subsurface oxygen dynamics can be developed and tested.

9:40am **SS+AS+TF-MoM-5 In-Situ Characterization of O_2 Gas-Induced Rearrangement of Near-Surface Composition in Refractory High-Entropy Alloys***, H. Kersell,* Oregon State University*; X. Fan,* University of Tennessee Knoxville*; A. Herman,* Oregon State University*; Z. Lyu,* University of Tennessee Knoxville*; B. Steingrimsson,* Imagars LLC*; P. Liaw,* University of Tennessee Knoxville*; **Gregory S. Herman**,* Oregon State University

Alloy formation enables the enhancement of material properties from electrical and thermal conductivity, to magnetism, chemical reactivity, and mechanical strength and ductility. For example, Ti alloys are lightweight, corrosion resistant, have low Young's modulus, and possess tunable strength and ductility at high temperatures. Their corrosion resistance and low Young's modulus make them suitable for biomedical implants, while their light weight, tunable strength, and high working temperatures facilitate use in high-temperature applications. Traditional alloys often contain a principal metal comprising most of the alloy composition, with additional functionality (e.g., oxidation resistance) induced by minority components. In contrast, high-entropy alloys possess multiple principal components, and have recently attracted significant attention for their enhanced tunability and sometimes unexpected physical properties.

Using ambient pressure X-ray photoelectron spectroscopy (AP-XPS), we have probed the initial oxidation of $TiZrHfNb_{0.3}$ refractory high-entropy alloys (RHEAs). Sputter-cleaning the as-cast alloy in ultrahigh vacuum removes adventitious carbon and native oxides, revealing a metallic alloy containing metal carbide species through its bulk. Subsequent vacuum annealing from room temperature (RT) to 100° C enriches the near-surface carbide content. This near-surface carbide enrichment continues with increasing temperature, accompanied by the formation of surface hydrocarbon species. Meanwhile, the relative compositions of Ti, Zr, Hf, and Nb are stable across the same temperature regime in vacuum. Despite their thermal stability, freshly sputter-cleaned, metallic alloy surfaces exposed to 1 mTorr of O_2 gas become enriched by a near-surface layer of Hf- and Zr- oxides. At the same time, the carbide component is suppressed, and a metal-oxide interface, containing Ti- and Zr- oxides, appears within the XPS probing depth (~8 nm). Subsequent RT oxygen exposure at higher O_2gas pressures induces comparatively minor changes in the surface oxide layer composition.

These results reveal the formation and nature of a thin protective oxide layer at the $TiZrHfNb_{0.3}$ RHEA surface in response to mild oxygen pressures. We present these results in terms of the O_2 pressure/temperature parameter space and discuss implications for the $TiZrHfNb_{0.3}$ RHEA behavior.

10:00am **SS+AS+TF-MoM-6 Surface Faceting and Oxidation in Binary and Ternary Ni-Based Alloys***, **Devin Jessup**, K. Orson, Z. Harris, P. Reinke,* University of Virginia

Future-proofing materials against degradation and failure means designing alloy systems with corrosion resistance built-in, and this is especially important for alloys in extreme environments. Ni-based superalloys are alloyed with Cr, Mo, and W which help form protective layers that are highly corrosion resistant mostly due to chromia (Cr2O3) formation. On polycrystalline alloy surfaces a wide range of crystallographic orientations coexist and are defined by the individual grains. For these often highly stepped or kinked surfaces, a complex surface faceting results from the tendency to minimize the surface free energy leading to an alloy with variable and complex surface topographies. Prior research indicates that different oxide species will nucleate along specific orientations resulting in oxide layer heterogeneity, which can introduce points of failure in the protective layer. Our work focuses on how these differences in surface crystallographic orientation can result in changes in the nucleation and growth of NiO and chromia, whose growth is kinetically controlled under our oxidation conditions.

A Ni11wt%Cr6wt%Mo alloy sample with large grains up to 1 mm offering a wide array of crystallographic orientations was selected for characterization. Scanning Tunnelling Microscopy (STM), Electron Backscatter Diffraction (EBSD), and Scanning Electron Microscopy (SEM) are used to characterize the surface. The native oxide was removed by annealing to 640˚C, and the highly variable surface topography was studied over a range of grains catalogued by EBSD. The alloy shows several unique surface topographies which are controlled by crystallographic orientation. Several examples are included in the supplemental material, which include wave-like facet structures, sharply terminating saw-tooth facets, and flatter "matchstick" structures. These can be correlated with the Miller index of the underlying grain surface on the stereographic triangle. The surface morphology was quantified with respect to facet size, shape, heights, orientation, and spatial distribution. This analysis provided the Miller indices for all well-expressed facets. Grain orientations were matched with their surface structures through a combination of feature matching between SEM and STM imagery and Fast Fourier Transform analysis. Further work will observe oxide nucleation on these facets, and their impact on oxide formation and performance. Understanding these mechanisms will contribute to our understanding of how to design Ni-based alloys for the most stable protective layer.

10:40am **SS+AS+TF-MoM-8 Medard W. Welch Award Talk: Atomistic Simulations to Advance Surface Science***, **Susan Sinnott**[1],* Pennsylvania State University **INVITED**

Computational methods are useful tools in the investigation of atomic and molecular dynamics and associated mechanisms at surfaces and interfaces. Physics-based classical potentials are a class of computational method that is useful for use in classical atomistic simulations of systems made up of thousands to many billions of atoms. These potentials consist of parameterized functions that capture aspects of atomic and molecular interactions within these material systems.

The focus of this presentation is on the third-generation charge-optimized many body (COMB3) potential. COMB3 was developed to enable an atomic-scale description of systems that include combinations of metallic, ionic, and covalent bonding under the same framework. The framework enables the system to determine the charge state of an atom or ion and manifest the physically appropriate type(s) and strength of local bonding as a function of environment correctly and autonomously. The framework further includes a combination of atomic-specific, bond-specific, bond-angle-specific parameters; the former is the same regardless of material, and only new bond-specific and bond-angle-specific parameters are required to extend existing elements to new compounds.

This presentation will provide an overview of the COMB3 potential and illustrate its utility in the study of water-metal surface and nanoparticle interactions, the examination of carbon nanoparticle-metal surface interactions, and the mechanisms associated with the growth of metal films on metallic and oxide substrates.

11:20am **SS+AS+TF-MoM-10 STM Study of Ag Encapsulation of Pd and Pt Islands on Ag(111) at Room Temperature***, **Buddhika Alupothe Gedara**[2], M. Trenary,* University of Illinois - Chicago

PdAg and PtAg bimetallic catalysts are used in many important industrial applications. Therefore, an atomic scale understanding of these catalysts is important for their further development. In this study, the initial stages of submonolayer growth of Pd and Pt islands on Ag(111) at room temperature were investigated using scanning tunneling microscopy (STM). Although Pd (1.7 J m^{-2}) and Pt (2.2 J m^{-2}) have higher surface free energies than Ag (1.1 J m^{-2}) and a similar lattice mismatch (PdAg = 4.8% and PtAg = 4.2%), Pd and Pt show different behavior after deposition on Ag(111) at room temperature. Hexagonal Pd islands are formed on Ag(111) regardless of the coverage. In contrast, Pt shows a high density of small clusters and larger islands indicating less mobility for Pt than Pd on Ag(111). Due to Pd atom place exchange with Ag atoms, Pd-rich brims were observed at the ascending Ag step edges. But, Pt-rich brims were not observed. Because of the absence of Pt-rich brims , removal of Ag atoms created bays at the step edges. Surface Ag atoms migrate to cover both Pd and Pt islands, even at room temperature, creating vacancy pits on the Ag(111) surface. In

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

[2] **SSD Morton S. Traum Award Finalist**

addition to large vacancy pits, small mobile vacancy pits were observed on Pt/Ag(111). Pd and Pt islands show different moire structures on Ag(111) even though they have almost same lattice mismatch. Migrated Ag atoms nucleate near the center of Pd islands to grow the second layer, whereas, migrated Ag atoms nucleate at the corner of the Pt islands.

Thin Films Division
Room 316 - Session TF+EM-MoM
Microelectronics and Spintronics Application

Moderator: John F. Conley, Jr., Oregon State University

8:20am **TF+EM-MoM-1 Rare Earth Thin Oxide Films for Sustainable Energy**, ***Ivona Z. Mitrovic***, *H. Finch, S. Almalki, S. Tekin, L. Jones, V. Dhanak,* University of Liverpool, UK*; A. Hannah, R. Valizadeh,* STFC Daresbury Laboratory, UK*; A. Renz, V. Shah, P. Gammon, P. Mawby,* University of Warwick, UK **INVITED**

An ever-greater impetus towards global net zero by 2050 has been driving research in sustainable electronics. This talk will give overview of research led at Liverpool on oxide thin films to be considered as high dielectric constant (high-k) dielectrics on (i) wide band gap (WBG) semiconductor materials for power electronics applications; and in (ii) metal-insulator-metal (MIM) configurations as rectifiers in infrared frequency rectennas for energy harvesting. The WBG semiconductor materials such as GaN and 4H-SiC have emerged as contenders to replace Si in many power electronics applications. High-k oxide materials are necessary for improved electrostatic control over the channel and improved on-current, which in-turn results in higher transconductance for GaN based Metal-Insulator-Semiconductor High Electron Mobility Transistors (MIS-HEMTs). Furthermore, the use of SiO_2 proves to be a bottleneck in exploiting full potential of SiC technology largely due to the unavailability of a reliable high-k dielectric alternative. In this paper, the two rare earth oxide films, Y_2O_3 and Sc_2O_3, prepared by sputtering, have been investigated in terms of their band alignment and interface properties on both GaN and 4H-SiC substrates using variable angle spectroscopic ellipsometry and X-ray photoelectron spectroscopy. Furthermore, this study includes applicability of Sc_2O_3 for use in MIM diodes for rectenna. The comparison to state of the art devices that mainly include Al_2O_3 and HfO_2 films has been discussed with the aim of paving the way forward for rare earth thin oxide film applications in driving sustainable future.

Acknowledgement. The UKIERI IND/CONT/G/17-18/18 and F.No.184-1/2018(IC) project funded by the British Council; UKRI GCRF GIAA award 2018/19, EP/P510981/1 and EP/K018930/1, funded by the EPSRC, UK.

9:00am **TF+EM-MoM-3 TaN Electrical Barrier for High-k MOS Capacitor**, *R. César,* ***José Diniz,*** University of Campinas - UNICAMP, Brazil*; R. Cotrin, E. Joanni, M. Vidal,* Renato Archer Information Technology Center, Brazil

Tantalum nitride (TaN) thin films were used at the interface between high-k titanium oxide (TiO_2) and the silicon substrate. The TaN films were deposited by RF sputtering and three thicknesses 2, 4 and 6 nm were studied. The structural characterization of the films was performed AFM, SEM and EDS. Using the AFM and SEM technique, it was possible to note that the film is formed by different grain sizes (Annex Fg.1). Using the EDS technique, it was possible to map the chemical elements that make up the TaN film, and it was possible to determine that 93,4% of the TaN film is composed of tantalum and 6,6% is composed of nitrogen.

MOS capacitors were developed using n-type silicon and TiO_2 as the gate dielectric. This oxide was deposited by ALD and has a thickness of 35 nm. Between the oxide and the silicon, TaN was deposited by RF sputering and has a thickness of 2, 4 and 6 nm. These devices have the upper electrode in the square shape and varying its dimension. Tables 1 and 2 in the Annex present the parameters calculated and extracted from the CxV and IxV curves of the MOS capacitors with TaN/TiO_2.

The capacitor with 6 nm of TaN did not present well-defined electrical measurements. This may be due to its thickness which started to act as a resistor between the TiO_2/Si. It can be seen from Tables 1 and 2 (Annex) that, 4 nm of TaN showed higher V_{FB} values than the capacitors with 2 nm of TaN. As seen in the structural characterization of the TaN films, the film has 93.4% tantalum. This metal ion is acting as a potential barrier on the capacitor. The higher the barrier, the higher the voltage must be for the device to work.

The capacitor with 2 nm of TaN showed higher hysteresis values than the 4 nm film, as shown in Tables 1 and 2. The 2 nm and 4 nm TaN capacitors showed $C_{máx}$ in the order of e^{-4} ~ e^{-5} F and e^{-4} ~ e^{-6} F, respectively. The same behavior can be described for $C_{mín}$ values. Both capacitors showed minimum capacitance on the order of e^{-5} ~ e^{-6} F.

Both capacitors presented effective charge density (Qo/q) in the order of e^{17} ~ e^{20} /cm^2. This result confirms that tantalum metal ions from the TaN film are interacting with the silicon substrate. Confirming the changes in the values of V_{FB}, $C_{máx}$ and $C_{mín}$. This indicates that variations in the dipole are occurring at the TiO_2/TaN/Si interface, due to chemical reactions between the two materials. These variations in the dipoles can change the value of the flat band voltage making it positive, which is the case for the two TaN film capacitors.

9:20am **TF+EM-MoM-4 Internal Photoemission (IPE) Spectroscopy Measurement of Interfacial Barrier Heights in Pristine and Poled Ferroelectric Hafnium Zirconium Oxide Devices**, ***Jessica Peterson,*** Oregon State University*; T. Mimura,* Gakushuin University, Japan*; J. Ihlefeld,* University of Virginia*; J. Conley,* Oregon State University

Ferroelectric $Hf_{0.5}Zr_{0.5}O_2$ (HZO) has attracted interest for CMOS memory and logic due to ease of integration as HfO_2 is already widely used. After device preparation, a "waking" process involving repeatedly sweeping a field across the material is necessary to induce ferroelectric behavior.[1] Use of HZO in CMOS applications requires knowledge of interfacial energy barriers in the specific film stacks used. Internal photoemission (IPE) spectroscopy is the only method of measuring barrier heights in working devices. IPE measurements of energy barriers have been reported for as-deposited HZO.[2] Here we investigate how waking and poling impact barriers.

20 nm thick HZO was deposited on a TaN coated Si substrates via atomic layer deposition (ALD) using 102 supercycles of HfO_2 (TDMAH) and ZrO_2 (TDMAZ), then coated with a 20 nm blanket TaN film and annealed at 600°C for 30 seconds. The top TaN layer was then stripped before depositing an optically transparent top electrode of 5 nm TaN / 5 nm Pd. Devices were woken by performing 5000 ±5V cycles. Woken devices were poled by applying a 0 to +4V or 0 to -4V square pulses. IPE measurements were taken by applying a voltage to the bottom electrode while grounding the top electrode. Positive (negative) polarity was used to assess the top (bottom) barrier. At each applied field, $\mathcal{E}_{app}$, photon energy incident on the top electrode was swept from 2 to 5 eV. Extracted spectral thresholds were plotted vs. $\mathcal{E}^{1/2}$ and extrapolated to zero field to account for any Schottky field induced barrier lowering.

For unwoken devices, the top and bottom HZO/TaN barriers were 2.6 and 2.9 eV, respectively, indicating the influence of processing. The waking process caused an increase in the top barrier to 2.9 eV while the bottom barrier was unchanged within error. Positive poling caused a reduction in both top and bottom barrier heights to 1.9 and 2.5 eV, respectively, for positive sweep first. Negative poling caused a reduction in top and bottom barrier heights to 2.1 and 2.2 eV, respectively, for negative sweep first. While field sweep direction did not impact barrier heights on pristine devices, it did have a small impact on poled devices, to be discussed. The lower barrier heights for poled devices and polarity dependence are consistent with a recent report on the impact of cycling on TiN effective work function on HZO, and suggest a role for oxygen vacancy migration.[3] This work provides insight into the impact of waking and poling on barriers in HZO devices, information needed for integration.

[1] Grimley et al., AEM 2, 1600173, (2016).

[2] Jenkins et al., ACS AMI 13, 14634 (2021).

[3] Hamouda et al., APL 120 202902 (2022).

11:00am **TF+EM-MoM-9 On-Chip ALD LiPON Capacitors for High Frequency Application**, *K. Ahuja,* University of Maryland, College Park*; V. Sallaz, F. Voiron,* Murata, France*; P. McCluskey, G. W. Rubloff,* University of Maryland, College Park*;* ***Keith E. Gregorczyk,*** University of Maryland

The increase in demand for miniaturized portable electronics has led to increased use of capacitors for power conditioning applications. In order to increase the efficiency of the electronic circuits, the ICs embedded in these devices require stable DC supply voltage, this requires optimization of power distribution networks (PDN). A common approach consists of placing a decoupling capacitor close to the ICs thus shorting the inductive path that limits the current flowing from the slow and distant battery and thus increasing the efficiency of the system. The traditional aluminum electrolytic capacitors and MLCCs are used for this application but they are limited by high intrinsic parasitic inductance, bulky volume, rigid shapes, and low energy density. Next-generation devices with solid-state electrolyte (SSE) using atomic layer deposition (ALD) provide a few

advantages to such applications. (1) Thin, ionically conductive materials allow for significant device dimensions reduction avoiding the above-mentioned problems, (2) easy integration with semiconductor chip manufacturing, and (3) an active community developing new materials regularly.

Here, we demonstrate ALD of ultra-thin film lithium phosphorus oxynitride (LiPON) as an inorganic SSE exhibiting both EDLC and electrostatic behavior. Two polymorphs of ALD LiPON ($Li_{3.47}PO_{3.43}N_{0.24}$ and Li_2PO_2N) are deposited between gold current collectors on silicon wafers. The ionic conductivity of the polymorphs is 6.82× 10^{-8} S/cm and 5.42× 10^{-7} S/cm respectively. The ionic conductivity was determined to be the most important metric effecting the charge storage mechanism. Both the LiPON capacitors exhibit an electric double layer behavior with a capacitance of 15 uF/cm^2 and a low leakage current (<20 nA/cm^2) at 2V. The $Li_{3.47}PO_{3.43}N_{0.24}$ shows EDLC behavior up to 1 kHz at 55°C whereas the Li_2PO_2N shows a similar behavior up to 10 kHz. Beyond this frequency, both the polymorphs show an electrostatic behavior with a high dielectric constant (13).

These results highlight the advantage of ALD LiPON as thin-film SSE for capacitors that shows EDLC behavior to an extended frequency limit (10kHz) for state-of-the-art applications. The electrostatic behavior observed at high frequency (>10 kHz) further expands the application window for high-frequency decoupling applications. The high energy density and on-chip integration allow for easier process control and design flexibility for advanced PDN. Further, utilization of ALD's inherent conformality in 3D nanostructures can extend the reach of these solid-state ionic capacitors to increasing energy density metrics along with on-chip integration.

.

11:20am **TF+EM-MoM-10 Designer Heusler Half-Metals for Ultra-Fast Spintronics*, Avik Ghosh,*** University of Virginia **INVITED**

Heusler alloys have several interesting attributes, such as a practical realization of the Slater-Pauling rule for half-metallicity with nearest neighbor interactions. Using Density Functional Theory we scavenged through a large number (1359) of full, half and inverse Heuslers, verified their thermal (heat of formation) and chemical (complex Hull distance) stability, and identified multiple potential Slater-Pauling semiconductors and half-metals (e.g. Fe2MnGe, layered Fe1.5TiSb, Co1.5TiSn). In addition, we found some zero momentum half-metals with negative formation energy, materials that are potentially insensitive to magnetic fields while carrying substantive spin currents. Interestingly, uniaxial anisotropy is seen to be induced in some of the L21 and C1b Heuslers (e.g. NiMnSb, CoTiSn) adjoining MgO without losing their half-metallicity, yielding potential magnetic electrode materials with large ballistic tunnel magnetoresistances. Finally, spin flip scattering rates are calculated with KKR and ballistic currents using quantum kinetics, showing that some of these Heuslers have low spin damping, making them good potential candidates for supporting room temperature, ultra-small Neel skyrmions.

Manufacturing Science and Technology Group
Room 305 - Session MS+AP+AS+TF-MoA

Advanced Characterization and Metrology for 3D and ML for Microelectronics Materials Discovery

Moderators: Alain Diebold, SUNY Polytechnic Institute, **Jeremy Mehta**, U.S. Department of Energy

1:40pm **MS+AP+AS+TF-MoA-1 Semiconductor Metrology for Dimensional and Materials Scaling*, Bryan Barnes,*** NIST **INVITED**

Dimensional and materials scaling are two key drivers for advancing computational capabilities beyond the conventional scaling trends of the last several decades. Future device metrology solutions must be developed now without clarity as to which combinations of proposed architecture(s) and novel materials will prove best suited for integration into high-volume manufacturing. This presentation briefly reviews these possible pairings and the near-term and long-term metrology challenges as identified in the *IEEE International Roadmap for Devices and Systems*. As device dimensions further approach near-atomic and atomic scales, many of the several existing metrology techniques will face new tests, illustrated here using examples and solutions from our optics-based semiconductor metrology research. No single metrology technique can address all issues faced in modern process control and inspection; thus we address complementary techniques across semiconductor metrology are required to address dimensional and materials scaling

2:20pm **MS+AP+AS+TF-MoA-3 Towards a Digital Twin for Spatiotemporal Experiments*, Subramanian Sankaranarayanan,*** Argonne National Laboratory **INVITED**

We will present our ongoing efforts at creating a virtual platform or “DigitalTwin”, wherein the users can exhaustively explore experimental controls and obtain synthetic read-outs – a small subset that displays the most interesting physics and/or phenomena can be explored in the actual experiments. We take advantage of the fact that most experimentalspatiotemporally-resolved measurements at SUFs in real or reciprocal space can be derived from the accurate prediction of atomic configurations and their dynamical evolution across time- and length. We will use representative examples to demonstrate how Digital Twins can be utilized for accelerated materials discovery and design.

3:00pm **MS+AP+AS+TF-MoA-5 Autonomous Scanning Probe Microscopy: from Streaming Image Analysis to Learning Physics***, S. Kalinin,* ***Yongtao Liu,*** Oak Ridge National Laboratory **INVITED**

Machine learning and artificial intelligence (ML/AI) are rapidly becoming an indispensable part of physics research, with domain applications ranging from theory and materials prediction to high-throughput data analysis. However, the constantly emerging question is how to match the correlative nature of classical ML with hypothesis-driven causal nature of physical sciences. In parallel, the recent successes in applying ML/AI methods for autonomous systems from robotics through self-driving cars to organic and inorganic synthesis are generating enthusiasm for the potential of these techniques to enable automated and autonomous experiment (AE) in imaging.

In this presentation, I will discuss recent progress in automated experiment in scanning probe microscopy, ranging from real-time image segmentation to physics discovery via active learning. The applications of classical deep learning methods in streaming image analysis are strongly affected by the out of distribution drift effects, and the approaches to minimize though are discussed. I will further illustrate transition from post-experiment data analysis to active learning process, including learning structure-property relationships and materials discovery in composition spread libraries. Here, the strategies based on simple Gaussian Processes often tend to produce sub-optimal results due to the lack of prior knowledge and very simplified (via learned kernel function) representation of spatial complexity of the system. Comparatively, deep kernel learning (DKL) and structured Gaussian Processes methods allow to realize both the exploration of complex systems towards the discovery of structure-property relationship, and enable automated experiment targeting physics (rather than simple spatial feature) discovery. The latter is illustrated via experimental discovery of ferroelectric domain dynamics in piezoresponse force microscopy. For probing physical mechanisms of tip-induced modifications, I will demonstrate the combination of the structured Gaussian process and reinforcement learning, the approach we refer to as hypothesis learning. Here, this approach is used to learn the domain growth laws on a fully autonomous microscope. The future potential of Bayesian active learning for autonomous microscopes is discussed.

4:00pm **MS+AP+AS+TF-MoA-8 New in-Line Metrology for Advanced Semiconductor Nodes*, Cornel Bozdog,*** Onto Innovation **INVITED**

Scaling in Semiconductor Device Manufacturing means "more devices per unit area". The traditional "device shrink" scaling path was already replaced by "stack vertically" in non-volatile memory devices, now up to few hundred devices occupying the same real estate on the wafer, and growing. Gate all-around allowed logic devices to stack multiple transistors, and volatile memory is following suit. Different devices and sub-devices are now bonded together to further optimize scaling. To integrate, optimize and control the multi-thousand-step manufacturing line, in-line metrology plays the critical role. Here we will review the metrology challenges for Advanced 3D devices, present the latest advancements in traditional optical, scatterometry, electron-beam and atomic force techniques, and discuss novel x-ray, acoustic, and mid-IR metrology solutions that enable accurate profile reconstruction, in-device characterization and hybrid metrology schemes.

4:40pm **MS+AP+AS+TF-MoA-10 Applications of Artificial Intelligence AI and Machine Learning ML to Semiconductor Materials Discovery and Optimization*, Brian Valentine,*** DOE **INVITED**

Semiconductor elements such as silicon and gallium are applied in a wide variety of electronic, optical, and energy conversion applications; new elemental, compound, and dopant compositions are continually sought to improve known semiconductor characteristics to find unknown but desired semiconductor material characteristics. In this paper some applications of AI and ML to semiconductor material design and optimization are reviewed, along with limitations of AI and ML techniques applied to materials design and development and forward directions in these materials design and development methods.

Thin Films Division
Room 316 - Session TF+EM-MoA

Thin Films for Optics, Photonics, Metamaterials, and Soft Electronics

Moderator: April Jewell, Jet Propulsion Laboratory

1:40pm **TF+EM-MoA-1 Strategies for Achieving Tunable Infrared Emission in III-V Materials*, Michelle Povinelli,*** *H. Chae, A. Ghanekar, B. Shrewsbury, R. Ahsan, R. Kapadia,* University of Southern California **INVITED**

We investigate strategies for creating tunable thermal emitters in III-V platforms. Two fabrication approaches are examined: direct growth of III-V films on metallic substrates and epitaxial transfer. We design corresponding infrared metamaterials and measure their wavelength-dependent absorptivity using FTIR spectroscopy. We demonstrate electrically induced shifts in the absorptivity spectrum. We then introduce device designs for absorptive/emissive switching. We assume that the applied voltage induces a perturbative index shift with double the period of the initial metamaterial. With careful design, the perturbation is predicted to switch the thermal emission on and off within a specified bandwidth and angular range.

2:20pm **TF+EM-MoA-3 Effects of Ultra-Thin Conformal Coatings on the Spectral Location of Reciprocal Plasmonic Metasurface Resonances*, Micheal McLamb,*** *V. Stinson, N. Shuchi, G. Boreman, T. Hofmann,* University of North Carolina at Charlotte

Optical metamaterials are a group of engineered materials that are composed of an arrangement of artificial structures, which result in properties that are not exhibited in naturally occurring compounds. These unique optical properties can be used to produce extraordinary optical effects including narrow band filtering [1], perfect lensing [2], and perfect absorption [3].

In order to achieve perfect absorption, metamaterial designs that rely on heterostructures have shown promising results [3, 4]. Heterostructured materials are composed of multiple, stratified constituents. We have developed a reciprocal plasmonic metasurface that is composed of two plasmonic metasurfaces with reciprocal surface geometries that are separated by a dielectric spacer. Experimental infrared reflection

measurements revealed the expected reciprocal plasmonic metasurface resonance, which was observed for the investigated geometries, at 4.8 µm. The location of this resonance was in agreement with finite element calculations.

We have also explored the optical response of reciprocal metasurfaces when coated with a conformal dielectric, amorphous Al_2O_3, for different coating thicknesses: 10 nm, 20 nm, 30 nm, and 40 nm. In order to experimentally explore the effect of ultra-thin conformal dielectric coatings on the spectral location of the reciprocal plasmonic metasurface resonance, Al_2O_3 coatings were deposited using atomic layer deposition. Our observations indicate that such dielectric coatings can induce a spectral red-shift of the main resonance of the reciprocal plasmonic metasurface allowing for the tuning of the resonant frequency.

1. V.P. Stinson, S. Park, M. McLamb, G. Boreman, and T. Hofmann, Optics, **2**, 284-291 (2021).

2. J.B. Pendry and S.A. Ramakrishna, Physica B, **338**, 329-332 (2003).

3. Y. Li, M. McLamb, S. Park, D. Childers, G.D. Boreman, and T. Hofmann, Plasmonics, **16**, 2241-2247 (2021).

4. M. McLamb, S .Park, V.P. Stinson, Y. Li, N. Shuchi, G.D. Boreman, and T. Hofmann, Optics, **3**, 70-78 (2022).

2:40pm **TF+EM-MoA-4 Integrating Structural Colors with Additive Manufacturing Using Atomic Layer Deposition***, **Tae Cho**, B. Rorem, N. Farjam, J. Lenef, K. Barton, J. Guo, N. Dasgupta,* University of Michigan, Ann Arbor

Structural colors, which allow for tunable surface reflectance spectra, are being increasingly used in a variety of applications such as optical displays, prints, decorations, and color photovoltaics. Compared to pigment-based colors, structural color offers many advantages including high brightness, durability, environmental sustainability, and ease of fabrication. However, traditional thin-film deposition processes often suffer from conformality, thickness control, and versatility in material selection. Compared to these techniques, atomic layer deposition (ALD) offers unparalleled control of film thickness and uniformity on complex topologies at relatively low temperatures which is compatible with polymer/biological/organic substrates. In this work, we fabricated asymmetric metal-dielectric-metal (MDM) structures which were sequentially deposited with nickel, zinc oxide (ZnO), and copper layer to form optical cavities. The ZnO thickness was varied from 40 nm to 160 nm which exhibited a full-color cycle from red, blue, and to yellow which agreed with the simulated spectra using the transfer matrix method.

To demonstrate the power of ALD to enable uniform and tunable coloration of non-planar three-dimensional objects, ALD MDM structures were deposited on 3-D printed metal objects. Blue and yellow colors were 'painted' onto the 3-D printed surface using 80 nm and 120 nm thick ALD ZnO, respectively, with 20 nm thick copper top layer. Vibrant and uniform colors were observed across all of the curved features owing to ALD's conformal coating of the microscopic porous topologies from metal 3-D printing.

Furthermore, our previous work has shown that using electrohydrodynamic jet (e-jet) printing, we can locally activate/passivate ALD growth for area-selective ALD (AS-ALD) patterning down to approximately 300 nm resolution [1]. By using e-jet printed patterns to control AS-ALD, multiple colors were printed on the same substrate by patterning the polymer inhibitor layers. This enables color printing of functional ALD materials with resolutions well below that of ink-jet printing. By combining AS-ALD with structural color, this work can open up the possibility of integrating additive nanomanufacturing with structural colors into even more complex 3-D geometries including hierarchical architectures that span nano- to macro-length scales.

[1] T.H. Cho, N. Farjam, C. R. Allemang, C. P. Pannier, E. Kazyak, C. Huber, M. Rose, O. Trejo, R. L. Peterson, K. Barton, N. P. Dasgupta, *ACS Nano* **14**, 17262 (2020)

[2] B. A. Rorem, T. H. Cho, N. Farjam, J. D. Lenef, K. Barton, N. P. Dasgupta, L. J. Guo, *Submitted* (2022)

3:00pm **TF+EM-MoA-5 Biosensor Encapsulation via Photoinitiated Chemical Vapor Deposition (piCVD)***, **Ruolan Fan**, T. Andrew,* University of Massachusetts - Amherst

Thin and porous poly(hydroxyethyl acrylate) (pHEA) and poly(3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooctyl acrylate) (pTFOA) encapsulating layers were successfully deposited on model electrical and optical glucose sensors via photoinitiated chemical vapor deposition (piCVD). This surface-restricted chain growth process afforded uniform coverage and strong interfacial adhesion of the resulting polymer encapsulation layers, which enabled the whole sensing area to be fully covered, even after being subjected to numerous electrochemical scanning cycles. Meanwhile, the amorphous films allowed rapid ion and analyte diffusion through themselves and, therefore, achieved quick sensing responses. Especially, pTFOA promised well-defined calibration curves with good repeatability. Furthermore, piCVD films maintained their morphology after being dehydrated and rehydrated over multiple days demonstrating their excellent stability as surface protective layers. These promising features of pHEA and pTFOA synthesized via piCVD may serve as a new encapsulating idea to be applied to various wearable sensors with different substrates and serve as a new strategy to extend the shelf life and functionality of biosensors.

3:20pm **TF+EM-MoA-6 Harnessing Wide-Range, Highly Stable Pressure Sensitivity Via PEDOT-Cl Vapor Printed Textiles for Health Monitoring***, **S. Zohreh Homayounfar**, A. Kiaghadi, D. Ganesan, T. Andrew,* University of Massachusetts, Amherst

The advancement of wearable electromechanical sensors to detect biopotentials and body locomotion is critically important in evaluating human performance and improving off-site care applications. The practicality of most of the so-far-developed sensors is highly restricted by the small range of detection and low stability against aging phenomena such as cycling abrasions, exposure to perspiration, and washing. By vapor deposition of a p-doped conjugated polymer, poly(3,4-ethylene dioxythiophene): chloride (PEDOT-Cl), we introduce an ultra-stable pressure sensor that reveals high sensitivity in detecting real-time signals in such a wide range of pressures that have not been reported before (from heartbeats to more than bodyweight). We leveraged a multi-scale working mechanism by developing two sensors: one with PEDOT-Cl coated cotton fabric and one with PEDOT-Cl coated cotton ball as the active layer. In addition to having percolation on the microscale, our sensors harness piezoionic effect on the nanoscale, which means that the redistribution of ions under the applied mechanical stress leads to the change in resistance. We protected the sensor against all the humidity-induced degradations entangled with ions and other aging processes via vapor deposition of hydrophobic moieties on all the sensor layers. With this protective coating, the sensor shows less than no change in resistance and sensitivity after staying in ~100% humidity for more than 150 hrs and can stand more than 10 laundry cycles without any drop in signal quality. Also, it displays ultra stability with 99.1% over 70,000 bending cycles in ambient conditions. The broad ability of this sensor was further confirmed by acquiring physiological signals and body motions such as heartbeats, respiration, and Joint movements. All these properties, along with the low-cost and robust fabrication process, bear the testimony that this sensor will be uniquely placed in wearable health monitoring electronics for both diagnostic and treatment applications.

Atomic Scale Processing Focus Topic
Room 317 - Session AP+AS+EM+HI+PS+SS+TF-TuM

Area Selective Processing and Patterning II

Moderators: Michelle Paquette, University of Missouri-Kansas City, **Christophe Vallee**, SUNY College of Nanoscale Science and Engineering

8:00am **AP+AS+EM+HI+PS+SS+TF-TuM-1 New Precursors and Approaches to ALD and AS-ALD of Metals*, Mikko Ritala,*** University of Helsinki, Finland **INVITED**

Metal ALD is a topic where high technological relevance combines with inspiring and challenging scientific questions. As always, the success of ALD builds on chemistry. There is constant need for new precursors enabling ALD of metals of interest with improved characteristics. A major challenge arise from the strong tendency of metals to agglomerate, hence preventing achieving continuous films at the smallest thicknesses. Lowering of the deposition temperature is of utmost importance to limit the agglomeration. This requires highly volatile and reactive metal precursors and reducing agents. 1,4-bis(trimethylgermyl)-1,4-dihydropyrazine ((Me_3Ge)DHP) is a new reducing that is found more efficient than its earlier reported silicon analogue. $NiCl_2(PEt_3)_2$ in turn represents a series of metal halide adduct compounds of nickel and cobalt where the poorly volatile parent halides are made volatile by proper adduct ligands. The $NiCl_2(PEt_3)_2$ - (Me_3Ge)DHP combination affords deposition of Ni at 110 °C which is the lowest temperature for thermal ALD of Ni so far. (Me_3Ge)DHP enables also deposition of gold. This is the first reductive thermal ALD process of gold.

Area-selective ALD of metals is an important topic for self-aligned thin-film patterning. An entirely new approach to this is area-selective etching of polymers. In these etching processes the selectivity arises from the materials underneath the polymer layers. Both O_2 and H_2 can be used as an etchant gas. Etching gas molecules diffuse through the polymer film, and if they meet a catalytic surface underneath, the molecules become dissociated into their respective atoms which then readily react with the polymer etching it away. On noncatalytic surfaces the polymer film remains. When combined with area-selective ALD, self-aligned etching of polymers opens entirely new possibilities for the fabrication of the most advanced and challenging semiconductor devices. An example is given where the area-selective etching of polyimide from Pt was followed by area-selective ALD of iridium using the patterned polymer as a growth-inhibiting layer on SiO_2, eventually resulting in dual side-by-side self-aligned formation of metal-on-metal and insulator (polymer)-on-insulator.

8:40am **AP+AS+EM+HI+PS+SS+TF-TuM-3 Comparing Interface and Bulk Physicochemical Properties of TiO_2 Deposited by PEALD Assisted by Substrate Biasing on Thermal SiO_2 and TiN Substrates, for Area Selective Deposition Application*, Jennifer Not,*** LTM - MINATEC - CEA/LETI, France*; L. Mazet,* STMicroelectronics, France*; T. Maindron,* Minalogic, France*; R. Gassilloud,* CEA-LETI, France*; M. Bonvalot,* LTM - MINATEC - CEA/LETI, France

To bypass the limitations implied by the miniaturization of electronic components, area selective deposition (ASD) is becoming a key point of focus, as photolithography steps are avoided. This bottom-up promising technique, as opposed to the top down approach inherent to etching, relies on nucleation mechanisms resulting from substrate - precursor interactions. Differing nucleation kinetics may indeed be observed under very same experimental conditions,[1] allowing a growth delay on a surface type while simultaneously promoting growth on a different surface.

Atomic Layer Deposition (ALD) remains a technique of choice to obtain area selective deposition. Based upon the self-limiting nature of surface reactions, this technique enables a conformal deposition with atomic-scale thickness precision, and is gradually becoming a major deposition process in the microelectronic industry.

The ALD reactor used in this study includes an ICP deported plasma source and is equipped with an additional RF polarization kit at the back side of the chuck, enabling plasma ion extraction from the source towards the substrate surface. Depending on the ion incident kinetic energy, which can be tuned as a function of the applied polarization bias, this ion flux can modulate the properties of the thin film under growth, opening new perspectives of physicochemical properties. These properties may also vary according to the substrate surface, making this RF polarization kit an interesting experimental knob for the development for ASD processes[2].

PEALD TiO_2 layers of various thicknesses have been deposited with no air break on a 15 nm-thick TiN layer, as well as on a 100 nm-thick thermal SiO_2 substrate, under various polarization bias power from 0 W to 80 W. The purpose of this work is to physically and chemically characterize the obtained thin films with respect to substrate surface, and to understand how these properties evolve with the film thickness and for various bias values. X-Ray Reflectivity (XRR), Grazing Incident X-Ray Diffraction (GIXRD), *in-situ* and *ex-situ* ellipsometry and Angle Resolved X-ray Photoelectron Spectrometry (AR-XPS) measurements have been performed, providing detailed information on chemical bond formation during nucleation and within the bulk TiO_2 layer, and thin film physical properties, such as thickness, density, roughness and crystallinity. The outcome of this study gives some insight into the benefit of bias for area selective deposition of TiO_2 thin films on TiN against SiO_2.

References

1. C. Vallée, M. Bonvalot *et al.*, J. Vac. Sci. Technol. A 38(3) May/June **2020**
2. T. Faraz *et al.*, ACS Appl. Mater. Interfaces, 10, 13158−1318 (**2018**)

9:00am **AP+AS+EM+HI+PS+SS+TF-TuM-4 Area Selective Atomic Layer Deposition of SnO_2 as An Etch Barrier*, Xin Yang,*** University of Texas at Austin*; B. Coffey,* Lam Research Corp*; J. Ekerdt,* University of Texas at Austin

Reactive ion etching (RIE) is widely used in semiconductor nanofabrication processes since it can provide high etch rate, high selectivity, and high anisotropy. Traditional etch masks such as organic photoresists suffer from shortcomings such as low etch selectivity. Other material systems have been investigated to improve the selectivity. $Sn^{(0)}$-containing block copolymers were demonstrated as materials for nanolithographic applications.

Here we propose SnO_2 as a RIE etch mask in fluorine-based etching processes. Tin forms nonvolatile compounds with fluorine enabling tin to function as an etch mask. We establish processes that create SnO_2 grid patterns, which can be transferred into the Si native oxide substrate using SF_6 RIE. The concept is illustrated using a 1000-mesh copper TEM grid as an ultraviolet light shadow mask to generate patterns in polystyrene. SnO_2 patterns are achieved by area selective atomic layer deposition (ALD) using tetrakis(dimethylamino) tin(IV) and H_2O as ALD precursors on a Si native oxide at 170 °C. The selective growth can be directed by the hydrophilicity of the substrate surface. ALD growth of SnO_2 shows no nucleation delay on Si native oxide, which is hydroxylated. By coating the substrate with a polymer such as polystyrene (PS) the reactive sites can be passivated to accomplish selective growth. SnO_2 growth can be blocked up to 50 cycles on H-terminated Si(001), and 200 cycles on cured polystyrene and possibly beyond. Atomic force microscopy (AFM) results show that SnO_2 grown on native oxide has a low roughness of 75 pm, while SnO_2 grown on H-terminated Si has a relative higher roughness of 250 pm indicating a 3-D growth process. To create SnO_2 patterns 20, 50, and 100 ALD cycles of SnO_2 are selectively deposited onto Si native oxide with estimated SnO_2 thicknesses of 1.2 nm, 3 nm and 6 nm, respectively. Samples are then etched with SF_6 RIE for 30 s to 1 min at room temperature and 200 mTorr. AFM results show that SnO_2 grid patterns are transferred into the substrate with a depth of around 300 nm to 1 µm for all three samples. X-ray photoelectron spectroscopy results show that some SnO_2 is transformed into SnF_4 for 100 ALD cycle samples, while all of the SnO_2 is transformed into SnF_4 for 20 and 50 ALD cycle samples.

9:20am **AP+AS+EM+HI+PS+SS+TF-TuM-5 Selective Deposition Two Ways: Chemical Bath Deposition of Metal Sulfides on Organic Substrates***, T. Estrada, **Amy Walker,*** University of Texas at Dallas

Selective deposition has many technological applications. While area selective deposition (ASD) has been widely investigated using atomic layer deposition (ALD), there have been few studies of composition-selective deposition or ASD in which growth occurs at material boundaries. In this talk we shall illustrate these alternate selective deposition methods using two examples.

First, we demonstrate that the composition of tin sulfides is controlled by the bath pH and the interaction of sulfur-containing species with $-CH_3$, -OH and -COOH terminated self-assembled monolayers (SAMs). On -OH terminated SAMs, as the bath pH increases from 10 to 12, the tin sulfide

deposited changes from SnS_2 to Sn_2S_3. On -COOH terminated SAMs the deposit is S_2S_3 at pH 10 and SnS at pH 12. In contrast, on -CH_3 terminated SAMs the deposit changes from SnS at pH10 to Sn_2S_3 at pH 12. We attribute this behavior to a competition between the repulsion of the chalcogenide ions by the negatively charged carboxylic acid and hydroxyl terminal groups and an increase in chalcogenide ion concentration with increasing bath pH.

Second, we exploit the interaction of the chalcogenide ions with different SAM terminal groups to deposit CuS nanowires at the junction of micropatterned -OH/-CH_3 terminated SAMs. We term this method SEmiconductor Nanowire Deposition On Micropatterned substrates (SENDOM). In SENDOM the deposition reaction is kinetically favored on the -CH_3 terminated SAMs but transport of reactants is preferred on the hydrophilic -OH terminated SAM. Thus at short deposition times a nanowire forms at the junction of the -OH and -CH_3 terminated surfaces.

9:40am **AP+AS+EM+HI+PS+SS+TF-TuM-6 Anatase Crystalline Phase Discovery on Ultra-Thin Layer TiO2Films During Low-Temperature Ald on Fluorine-Rich Carbon Substrates***, **Brian Butkus**, S. Dabas, C. Feit, J. Ganesan, Z. Parsons, X. Feng, P. Banerjee,* University of Central Florida

A novel approach to crystalline anatase phase in atomic layer deposition (ALD) of $TiO_2$by deposited on a fluorine-rich carbon substrate using titanium (IV) isopropoxide (TTIP) and O_2 plasma. In films deposited at temperatures as low as 100 ºC and with a thickness of only 4 nm, highly crystalline anatase phases have been observed. Furthermore, when deposited on glass or silicon substrates other than carbon, TiO_2 films consistently produce amorphous films under these conditions. This talk will highlight the unique substrate-driven crystallization of ALD TiO2 and lays the ground rules for selective crystallization using surfaces with suitable initiation chemistries.

An ALD process using a Veeco® Fiji Gen2 ALD system was used to deposit TiO_2 on hydrophobic, polytetrafluoroethylene-coated carbon substrates (AvCarb GDS2230 from Fuel Cell Store). Temperatures of the ALD ranged from 100 ºC to 200 ºC, and O_2 plasma (300 watts) and water were used as oxidants. Target film thickness ranged from 4 nm to 22 nm. To characterize the films, Raman, Fourier transform infrared spectroscopy (FTIR), and x-ray photoelectron spectroscopy (XPS) were used. AvCarb GDS2230 substrates with an O_2 plasma as an oxidant resulted in anatase TiO_2 films irrespective of thickness, even when deposited at temperatures below 100 ºC. However, the anatase phase is significantly weaker when H_2O is used as the oxidant. An interfacial layer of ALD Al_2O_3 suppresses the growth of the anatase phase. Data from XPS indicates that Ti-F bonds form at the pre-deposition stages of films with anatase TiO_2. On non-fluorinated substrates, where the Ti-F bond does not exist, this structurally distinguishes amorphous TiO_2. This fluorine on the surface of the carbon paper serves as a directing agent[1-5] for the application of TTIP to PTFE in a flourolysis reaction, which drives the TiO_2 to crystallize into anatase films.

Fluorine doped crystallization in Ti-O systems has been reported in sol-gel and hydrothermal approaches to synthesize TiO_2 powders.[6, 7]Here, we report the first gas-phase analog of the above reaction mechanism to synthesize crystalline anatase TiO_2 films. With this strategy, surface initiation chemistries can be used to achieve area-selective and in situcrystallization of films.

11:00am **AP+AS+EM+HI+PS+SS+TF-TuM-10 Site-selective Atomic Layer Deposition: Targeting Electronic Defects***, **Alex Martinson**,* Argonne National Laboratory **INVITED**

While ALD is most commonly employed in uniform conformal growth, more selective precursors and processes may allow for more precise synthetic strategies including targeted reaction at subtly unique surface sites including those that lead to electronic defects. We apply a selective hydration strategy to target reaction at the step edges and/or oxygen vacancies of rutile TiO2 and In_2O_3. We computationally and experimentally investigate the feasibility of facet- and site-selective ALD through accurate asymmetric slab models from which the free energy of adsorption at unique surface sites is leveraged to predict step selectivity. Computational evaluation of ALD precursor adsorption free energies on multiple dehydrated facets further refine the feasibility of a temperature-dependent selective hydration strategy. Initial experiments of Al2O3 and Ga_2O_3ALD nucleation on TiO_2single crystals and MgO ALD on In_2O_3broadly support the computational predictions and strategy. The strategies outlined here provide one possible route to selectively target growth at structural defects of oxide surface that may also act as surface or interface electronic defects.

11:40am **AP+AS+EM+HI+PS+SS+TF-TuM-12 Low Temperature Area-selective ALD and ALE of Pd***, H. Nallan, X. Yang, B. Coffey, **John Ekerdt**,* University of Texas at Austin **INVITED**

Thin film deposition and etching approaches may be constrained by the temperature limits for flexible substrates in roll-to-roll processes.We describe a low temperature ALD route to Pd metal film growth at 100 °C that uses $Pd(hfac)_2$ and H_2.The Pd ALD reaction proceeds in the presence of atomic hydrogen; Pd growth nucleates without delay on a Ni metal seed layer that catalyzes H_2 dissociation.Once nucleated, the evolving Pd surface catalyzes H_2 dissociation.To generate the Ni seed layer, a NiO film is first deposited and reduced with an atomic hydrogen source. The 100 °C ALD of NiO using bis(N,N'-di-*tert*-butylacetamidinato)nickel(II) and H_2O as coreactants is highly selective on exposed oxide surfaces and blocked on organic surfaces.NiO films as thin as 0.5 nm, once reduced to Ni^0, effectively seed Pd growth through catalytic area activation.NiO reduction employs an e-beam heated tungsten capillary at 2.5×10^{-6} Torr H_2 that generates atomic hydrogen to reduce NiO films at 100 °C.

In the event non-selective nucleation occurs on passivated regions, we describe a low temperature ALE route to etch clusters/islands on the passivated regions faster than the desired film.This low temperature route exploits the general findings that metal oxides can be etched by a variety of vapor phase etchants, such as formic acid – the issue is controlled oxidation while minimizing damage to adjacent surfaces.We present a low temperature route that involves VUV ($115 \text{ nm} < \lambda < 180 \text{ nm}$) activation of O_2 to produce atomic oxygen and ozone, with atomic oxygen being the dominant species that oxidizes the near surface region of Pd at 100 °C.Oxidation extents differ between continuous films and discontinuous films enabling the removal of metal islands without significantly etching the film.Density functional theory is used to study the adsorption of oxidants (O and O_3) and describe O diffusion into the films to understand the kinetic limitations of the oxidation step.

Biomaterial Interfaces Division
Room 318 - Session BI1+AS+EM+NS+SE+TF-TuM

Bioanalytics, Biosensors and Diagnostics

Moderators: Caitlin Howell, University of Maine, **Laura Mears**, TU Wien, Austria

8:00am **BI1+AS+EM+NS+SE+TF-TuM-1 Understanding and Employing Adhesion Forces in Microfluidic Channels for Cell Separation***, **Avi Gupta**, F. Chrit, A. Liu, A. Alexeev, T. Sulchek,* Georgia Institute of Technology, USA

Rapid advancements in microfluidic technologies during the past few decades have significantly aided advancements in the field of BioMEMS. These technologies can facilitate development of easily scalable tools that can be translated to point-of-care healthcare products. Researchers have capitalized on these tools to create differential separation techniques that rely on adhesion forces. The adhesive interactions play a significant role in governing the trajectory of cells in microfluidic channels as well as the reliability of these devices, however, a concise model explaining cell interactions with chemically coated surfaces is yet to be developed. This research describes studies using microfluidic flow at different flow regimes to study dynamic cell adhesion. APTES, P-selectin, and Pluronic were used as models for non-specific adhesion, specific adhesion, and adhesion-free surfaces, respectively. A microfluidic device with slanting ridges was used to provide forced contact and to visualize the effect of these chemistries on cell trajectories using a microscope and a high-speed camera. Parameters of the channel that were studied include ridge angle, gap size, channel width, and flow rate. It was found that adhesive forces modulate the interaction time of cells during contact points with the slanting ridges. At an average flow velocity of 3.1 cm/sec we observed higher interaction time for APTES coatings and lower for Pluronic coatings. Higher adhesion on APTES coated surface of the channel leads to more deflection of cells towards the streamlines leading them to go opposite to the ridge direction. In contrast, lower surface adhesion on Pluronic coated surface made cells deviate along the ridge perpendicular to streamlines. Narrow channel widths and acute ridge angles helped in exaggerating the differences in trajectories of cells going along or under the ridge. Atomic force microscopy (AFM) was used to quantify the adhesion forces. This knowledge was used to develop a predictive model employing Lattice Boltzmann techniques along with Morse potential and Bell model to represent interaction between cells and device surface. This improved understanding of adhesion forces in microfluidic devices opens new avenues for developing separation techniques that don't employ specific

molecules like P-selectin but rely upon the inherent geometry and surface interaction of the cells with a microfluidic channel.

8:20am **BI1+AS+EM+NS+SE+TF-TuM-2 Wafer-Scale Metallic Nanotube Arrays with Highly Ordered Periodicity for SERS Application**, ***Jinn Chu***, National Taiwan University of Science and Technology, Taiwan

This paper reports on the wafer-scale fabrication of ultrahigh sensitivity SERS substrates using metallic nanotube arrays (MeNTAs) with highly ordered periodicity. Various metals and alloys have been used to prepare MeNTAs via sputtering over a contact-hole array template created in photoresist. These include ferrous (stainless steel) and nonferrous (Cu-, Ni-, Al-, and Ti-based) alloys, as well as elemental metals (Cu, Ag, and Au). The proposed nanotubes can be fabricated over a wide range of heights and diameters (from a few hundred nm to 10 µm) in a variety of shapes, including tall cylinders and dishes. In addition, over this is deposited a uniform coating of Au nanoparticles to form a high-sensitivity AuNP@MeNTAs 3D-SERS substrate. Systematic micro-Raman spectroscopic analysis reveal that the fabricated array could function as a SERS-active substrate with crystal violet (CV) and folic acid as analytes (a minimum detection limit of 10^{-13} M CV). Enhancement factor of 1.06×10^9 is obtained from our triangular Ag MeNTA. This work is the first to fabricate wafer-scale metallic nanotube arrays with SERS properties, which represents an important step toward realizing the large-scale fabrication of ultrasensitive SERS-active materials.

8:40am **BI1+AS+EM+NS+SE+TF-TuM-3 Customizing Silk Film Surface Properties Using Plasma-Enhanced Chemical Vapor Deposition**, *A. Devore, G. Reyes, **Morgan Hawker***, California State University, Fresno

Silk fibroin (silk) is a naturally-derived polymer with high utility in biomedical contexts, notably in tissue engineering. Silk bulk properties can be tuned to mechanically match a range of biological environments, including soft and hard tissues. As with other naturally-derived polymers, silk constructs degrade via surface-mediated enzymatic hydrolysis into non-toxic amino acid byproducts. Because tissue engineering relies on the underlying scaffold to degrade as the healthy tissue forms, controlling silk scaffold degradation kinetics is essential to maximize silk's utility. Notably, prior work to control silk degradation kinetics relies on either altering silk matrix properties (i.e., manipulating the secondary structure), or through creating silk-containing blends such as copolymers. Although both strategies effectively control degradation, doing so is often at the expense of mechanical properties. Any mechanical mismatch induced through controlling degradation can hinder scaffold function. Developing a strategy to program silk degradation - without altering bulk mechanical properties - is required to enhance their efficacy as biomaterials.

This talk will highlight recent efforts to develop a radio-frequency plasma-enhanced chemical vapor deposition (PECVD) approach with the potential to modulate silk degradation. The long-term objective of this work is to control the rate of surface-mediated enzymatic hydrolysis by customizing silk surface properties. Surface properties are thought to be paramount in controlling silk construct/enzyme interactions, so tuning silk film surface properties using PECVD was a logical first step. Silk films were first dropcasted, and were then subjected to PECVD. Plasma feedgas composition was tuned using two unique precursors: acrylic acid (to produce thin films with polar functional groups on the silk surface), and pentane (to produce thin films with non-polar functional groups on the silk surface). Plasma polymerization using mixed precursor conditions was also explored. Contact angle goniometry was utilized to evaluate the wettability of all plasma-modified and control silk films. Changes in surface chemistry were evaluated using high-resolution x-ray photoelectron spectroscopy. Collectively, findings demonstrated that surface properties depend on both feedgas composition and position of the silk film in the plasma reactor. In sum, PECVD represents a promising approach to customize silk surface properties.

9:00am **BI1+AS+EM+NS+SE+TF-TuM-4 Biopotential Sensing Using Flexible, Reusable Smart Textile-Based Dry Electrodes**, ***Jitendra Pratap Singh***, Physics Dept IIT Delhi, India

Biopotential signals are used to assess organ function and make diagnoses. Biopotential electrodes are used to monitor and record biopotentials by acting as an interface between biological tissue and electrical circuits. The accurate detection of physiological signals from the human body is essential for health monitoring, preventive care, and treatments.

Wearable bioelectronics developments applied directly on the epidermal surface provide a promising future biopotential sensing option. Wearable textile electrodes for biopotential sensing are a promising candidate for long-term health monitoring. Wearable health-monitoring devices should be simple to use, stigma-free, and capable of delivering high-quality data. Smart textiles, which incorporate electronic elements directly into the fabric, offer a seamless way to incorporate sensors into garments for a variety of purposes. This work describes different types of flexible and reusable textile-based dry electrodes for biopotential monitoring. This work also describes the direct writing of laser-induced graphene (LIG) on a Kevlar textile for the production of reusable dry electrodes for long-term ECG monitoring. The electrode as-prepared has a high electrical conductivity and skin contact impedance of 100 ± 1 kΩ to 7.9 ± 2.7 kΩ for frequencies ranging from 40 Hz to 1 kHz, which is comparable to conventional Ag/AgCl wet electrodes.

The outcomes demonstrate comparable performance with significantly reduced electrode-skin impedance for clinical-grade devices. Even after several hours of usage, these electrodes do not irritate the skin and are effective without any skin preparation. As a result of their flexibility and a better match to the modulus of the skin, it is anticipated that the suggested dry electrodes will provide comfort for long-term biopotential monitoring. A simple, cost-effective, and scalable fabrication approach enables the fabrication of flexible electrodes of arbitrary shape for long-term biopotential monitoring.

1. Y. Maithani, B. Choudhuri, B. R. Mehta, and J. P. Singh: Self-adhesive, Stretchable, and Dry Silver Nanorods Embedded Polydimethylsiloxane Biopotential Electrodes for Electrocardiography. *Sensors Actuators A Phys.***332**, 113068 (2021).
2. Y. Maithani, B. Choudhuri, B. R. Mehta, and J. P. Singh: Modelling and Analysis of Active Biopotential Signals in Healthcare , Volume 2 A comprehensive review of the fabrication and performance evaluation of dry electrodes for long - term ECG monitoring. *IOP Publ. Ltd 2020***2**(chapter 8), 1 (2020).

9:20am **BI1+AS+EM+NS+SE+TF-TuM-5 Functional Plasma Polymers for Biosensing Applications**, ***Melanie McGregor***, University of South Australia **INVITED**

Materials with intricate nanostructures display wetting properties that modern technologies already use to lubricate engines or waterproof clothing. Yet, their full potential in applications for sustainable catalysis, air purification or biosensing cannot be realised until we understand how nano-objects adsorb to surfaces with features of comparable size. Indeed, controlling or even predicting how proteins, antibodies, exosomes, surfactant or nanoparticles stick to nano-engineered surfaces is a challenge because key aspects of the wetting phenomenon remain poorly understood at this scale. In this talk, I will briefly review what we currently know about "nanowetting".[1] I will then introduce the concept of plasma polymerisation as a technique to control both surface chemistry and surface topography. I'll use the example of plasma deposited polyoxazoline (POx) to highlight this technique's attributes, drawbacks and recent progress made in understanding the unique chemistry and reactivity of POx films, using both plasma in-situ and post deposition spectroscopic analysis.[2]Plasma deposited Polyoxazoline thin films share many valuable properties with polyoxazoline prepared via conventional organic chemistry: they are biocompatible, non-cytotoxic and low fouling.[3] What is more, they bind biomolecules covalently, support cell adhesion, and are generated in a solvent free, single step process, which makes them particularly attractive for industrialization. For these reasons, plasma deposited polyoxazoline are used in applied biomedical research, from in vitro stem cell culture to controlling immune responses.[4]

I'll conclude this presentation with tangible outcomes of the translational research projects I've conducted with various industries, where we used nanoengineered plasma polymers, to create materials for cancer diagnosis and growing organoids.[5]

[1]**M. MacGregor** and K. Vasilev. *Advanced Materials Interfaces,4*, 1700381.,2017**;M. MacGregor** et al., *Nanoscale*, 8(8),4635-4642, 2016

[2] **M. Macgregor***et al.*Chemistry of Materials, 29(19)8047-51,* 2017; **M. N. MacGregor**-Ramiasa et al., *J. Mat. Chem. B*, 3, 6327-6337, 2015

[3]**M. N. Ramiasa** et al. *Chem. Commun.*, 51, 4279-4282,2015**;**A. A. Cavallaro, **M. N. Macgregor**-Ramiasa, K. Vasilev, *ACS Appl. Mater. Interfaces8*, 6354, 2016.

[4] R. M. Visalakshan, A. A. Cavallaro, **M. N. MacGregor**, et al. *Adv. Funct. Mat.*, 29, 1807453, 2019**;**

[5]**M. MacGregor***et al. *Biosensors and Bioelectronics,* 171: 112699,2020; K.M. Chan […]**M. MacGregor****Cancers* 13(21), 5544 2021

Thin Films Division
Room 316 - Session TF-TuM

Growth in 3D, High Aspect Ratio and Nanostructured Materials

Moderators: Adriana Creatore, Eindhoven University of Technology, Netherlands, **Richard Vanfleet**, Brigham Young University

8:00am **TF-TuM-1 Tailoring 3-D Nanomaterial Architectures Using ALD: Bridging Scales from Atoms to Bulk***, **Neil Dasgupta,*** University of Michigan **INVITED**

As we move towards a vision of "materials by design" in the 21st century, the ability to rationally control hierarchical material architectures becomes increasingly critical. This is inspired by natural systems, which routinely achieve material properties that are not available in the bulk through precise ordering across several orders-of-magnitude in length scale. However, while there have been tremendous advances in self-assembly and additive manufacturing in three dimensions to create periodic structures such as meta-materials, as we move towards composite material architectures composed of multiple dissimilar materials, heterogeneous interfaces play an increasingly important role. In particular, integration of materials with significantly different mechanical, thermal, optical, and/or electronic properties into "bulk" hierarchical architectures requires atomically-precise and deterministic control of surfaces and interfaces.

In this talk, I will demonstrate examples of how Atomic Layer Deposition (ALD) is a key enabling technique to enable the rational design of hierarchical material systems. These atomically-precise surface modifications can be used to direct self-assembly processes, provide tunability of the optical, electronic, thermal, and mass transport properties of integrated material systems, and encapsulate structures to promote their stability in a wide range of environments. I will present examples of how ALD can enable hierarchically-structured materials by design, including three-dimensional solid-state batteries, photocatalysts for solar fuel conversion, multi-functional composites, and anti-fouling surfaces. I will further provide a perspective on how this versatile approach can lead to the design and scaled-up manufacturing of material systems with precision at length scales ranging from atoms to meters

8:40am **TF-TuM-3 Thin Film Technology and Diagnostics for Multilayered Solid-State Batteries***, **Victoria Castagna Ferrari**, G. Rubloff, D. Stewart,* University of Maryland, College Park

Thin-film solid-state batteries (SSBs) can provide high-power performance with easy miniaturization and on-chip integration, but broader applications demand higher energy density. Thin film fabrication enables new cell architectures to achieve this. Using sequences of in-situ patterning and deposition, we were able to produce a multilayered battery in a 3D architecture like a prismatic pouch cell. The advantages of such unique design are: i) individual solid-state batteries can be small (µm to cm scale) and shaped to fit the application while providing faster charge and discharge; ii) a multilayered stack, where the cathode and anode layers are connected on either sides in parallel, minimizes passive structural material, thereby improving the total device energy density; and iii) applying multilayer shadow masking during sputtering avoids high-aspect ratio deposition challenges.

Prototypes of this prismatic battery with 1 and 3 layers were made using the sputtering tool to judge the scaling of discharge capacity and power performance. Thin films of silicon, LiPON, and lithiated vanadium oxide (LVO) were deposited as the anode, electrolyte, and cathode layers to produce a battery with tunable lithium content, without breaking vacuum during the entire fabrication sequence. As a final step, the whole SSB stack was post-annealed at 300 °C. A single-layer prototype device with area 0.15 cm^2 and total battery thickness 1µm was electrochemically active when cycled between 0 and 4 V. Charge-discharge testing showed an initial capacity of 50 mAh/g under fast rate (5C) with a Coulombic efficiency of 98 %.

Our initial multibattery device, comprising a three-battery stack, revealed rougher interfaces and susceptibility to delamination. SEM-cross-sectional images showed unexpected voids in the LVO/LiPON interface, suggesting side reactions and possible additional lithiation of the LVO from the LiPON layer. Clearly, understanding and controlling interfaces will be crucial to multilayered thin-film batteries. Hence, we have conceived a new diagnostic platform for developing multilayer SSBs comprised of new shadow masks configured to characterize properties of each active layer and interface, as well as the entire multibattery device, using electrochemical impedance spectroscopy (EIS) and equivalent circuit modeling of the full battery and its constituent components. As a preliminary result, we found that the LVO/LiPON interface represents the largest contribution to the total cell impedance. As simultaneous high power and high energy drive multibattery SSB architectures, revealing properties of individual interfaces and layers will be crucial to success.

9:00am **TF-TuM-4 Interface Mixing in Thin-Film Solid-State Sodium Batteries***, **Blake Nuwayhid**, A. Kozen,* University of Maryland*; D. Long,* Air Force Research Laboratory, USA*; G. Rubloff, K. Gregorczyk,* University of Maryland

Nanostructured solid-state batteries (SSBs) are poised to meet the demands of next-generation energy storage technologies, with atomic layer deposition (ALD) being a powerful tool enabling high-performance nanostructured SSBs that offer competitive performance with their liquid-based counterparts. Furthermore, switching from lithium-ion batteries to those based on the more abundant sodium-ion charge carrier is an attractive route to decrease costs. Recently, we developed an ALD process for sodium phosphorus oxynitride (NaPON) as a solid-state sodium ion electrolyte.[1] NaPON proved to be an effective solid-state electrolyte (SSE) with an ionic conductivity of 1.0 x 10^{-7} S/cm at 25 °C and a wide electrochemical stability window of 0-6.0 V vs. Na/Na^+. In this presentation, thin-film solid-state sodium batteries are explored, in which NaPON is paired with a V_2O_5 cathode and a thermally evaporated Na metal anode. Electrochemical analysis of the SSB suggests intermixing of the NaPON/V_2O_5 layers during fabrication. We investigate this interfacial reactivity in three ways: with *in-situ* spectroscopic ellipsometry, time-resolved XPS depth profiling, and cross-sectional cryo-TEM. We characterize this reaction during the ALD NaPON deposition on V_2O_5 to be two-fold: (1) reduction of V_2O_5 to VO_2 and (2) Na^+ insertion into VO_2 to form Na_xVO_2. The Na metal evaporation process is found to intensify this reaction, resulting in the formation of irreversible interphases between discrete battery layers. Despite the mixed interphases formed during fabrication, the SSB can operate for over 100 cycles and represents the first demonstration of a functional thin-film solid-state sodium-ion battery. This work highlights the high reactivity of Na compared to Li-based battery chemistries, not only necessitating the need for interfacial coatings in Na-SSBs, but also helps to define design rules required during fabrication of Na-SSBs or liquid Na-ion batteries.

1. Nuwayhid, R. B.; Jarry, A.; Rubloff, G. W.; Gregorczyk, K. E., Atomic Layer Deposition of Sodium Phosphorus Oxynitride: A Conformal Solid-State Sodium-Ion Conductor. *ACS Applied Materials & Interfaces* **2020,***12* (19), 21641-21650.

9:20am **TF-TuM-5 Direct CVD Synthesis of MgH_2 Thin Films and Nanowires by Decomposition of the Novel Magnesium *Bis*-Diamidodiboranate Precursor***, **Laurent Souqui**, C. Caroff, S. Shrivastav, G. Girolami, J. Abelson,* University of Illinois at Urbana-Champaign

MgH_2 is a wide-bandgap light-weight dielectric which can be fully dehydrogenized to form metallic Mg above 410 °C. For these reasons, it has been extensively studied as a potential material for switchable windows and for hydrogen storage and fuel cells, and as a passivation layer for Si-based photovoltaic devices. Compared to common synthesis routes to MgH_2, such as high energy ball milling and liquid phase nanoconfinement, chemical vapor deposition (CVD) allows reduced synthesis time and process scalability with precise control of grain size and distribution to afford ultrathin layers. Unlike sputtering and evaporation, CVD is not a line-of-sight technique; at low deposition temperature, limited precursor reactivity produces highly conformal deposition on complex morphologies and structures. In the present work, a new CVD precursor, magnesium *bis*-diamidodiboranate ($Mg[N(Me)_2\text{-}BH_2\text{-}N(Me)_2\text{-}BH_3]_2$, $Mg(NBNB)_2$), was designed for clean reactivity at low temperatures. We report the direct synthesis of α-MgH_2 thin films by CVD from $Mg(NBNB)_2$ in the range 80-350 °C and 10-60 mTorr, affording growth rates of 1.9 to 11.3 nm/min. In contrast with earlier works, which utilized the composition of the gas phase

to infer the synthesis of MgH_2 from alkyl magnesium precursors, we document the formation of MgH_2 using thin film characterization techniques.

We found that only the mass-transport-limited regime could be accessed even at the lowest deposition temperature, indicating that the reaction sequence of the precursor with the growing MgH_2 surface has relatively low energy barriers. This is in contrast with the interaction of the precursor with the substrate surface, as a significant nucleation delay was observed, lasting from 7 min at 170 °C to 20 min at 350 °C. We suggest that this delay is due to an increasing desorption rate of the precursor, an increasing instability of initial nuclei or an increasing diffusion rate of Mg into the substrate. The crystallinity of the films was found to be independent of the temperature and was mostly affected by the precursor partial pressure. Above 170 °C the morphology of the films changes from granular to a percolated network of islands and nanowires grew extensively above 200 °C. These nanowires were found to be 50 nm in diameter, which makes them interesting for application in hydrogen storage. The refractive index and absorption coefficient were found to be dependent both on deposition pressure and deposition temperature, this behavior is attributed to the tendency of MgH_2 to form H vacancies at high vacuum and high temperature conditions.

9:40am **TF-TuM-6 The Fabrication of Heterojunctions by Atomic Layer Deposition for Gas Sensing Applications***, **Nicola Pinna**, H. Raza,* Humboldt University Berlin, Germany

Material and methods for detecting a wide range of harmful species are becoming increasingly necessary as automation and industrial growth increase. Chemoresistive gas sensors using semiconducting metal oxides (SMOX) are fundamental for developing efficient gas sensors. The sensitivity and selectivity of these nanostructured SMOX can be boosted by combining them with other SMOX. Yet control over the thickness of the shell layer is crucial; particularly, a thin shell layer modulates the space charge layer at the interface, thereby influencing effectively the charge conduction channel. The engineering of heterojunctions with well-defined core and shell layers is required to better understand the sensing response of heterostructured nanomaterials. A comprehensive understanding of the role of semiconductor heterojunctions and the sensing response of core-shell heterostructures is achieved by synthesizing a series of well-defined and well-controlled heterostructures with varying core and shell layers. NiO- and SnO_2-based hierarchical coaxial core-shell heterostructures are therefore proposed to achieve this objective. The designed heterostructures exhibit sensing responses related to the NiO or SnO_2-shell layers, or in some cases to the heterojunctions between $_n$SMOX (SnO_2) and $_p$SMOX (NiO). A comparison of the sensing response in order to understand the transduction mechanism across the interfaces in atomic layer deposition grown heterojunctions will be presented.

11:00am **TF-TuM-10 Tunable ALD Infiltration into High-Aspect-Ratio Aerogels Enabled by Process Modeling for Solar Thermal Applications***, **Andrew J. Gayle**[1], Z. Berquist, Y. Chen, A. Davoodabadi, A. Hill, J. Hoffman, A. Bielinski, A. Lenert, N. Dasgupta,* University of Michigan, Ann Arbor

ALD provides a unique opportunity to impart conformal surface functionalization onto ultra-high-aspect-ratio structures, but depositions are complicated by precursor diffusion and dosing limitations. ALD modifications on substrates such as aerogels help enable their use in fields such as concentrated solar thermal (CST), catalysis, and filtration. SiO_2 aerogels possess a unique combination of desirable properties for CST applications, including high optical transparency and low thermal conductivity, but they suffer from poor stability at elevated temperatures. In this work, we investigate the ALD conditions needed to conformally modify SiO_2 aerogel monoliths (AMs) with aspect ratios >60,000:1 [1]. To minimize precursor waste during the long diffusion times necessary to conformally modify the AMs, we implemented a multi-dose-quasi-static-mode (multi-dose-QSM) deposition procedure. In standard QSM recipes, reactor pumping is halted during an “exposure step”, allowing precursor to diffuse into a structure without being purged. In the multi-dose-QSM technique, multiple doses and exposure steps of a single precursor are implemented prior to dosing the counter reactant. This was necessary due to the large surface area of the AMs.

To enable tunable ALD infiltration depths into the AMs, we developed a model of the multi-dose-QSM deposition process. Our model accounts for precursor depletion in the ALD chamber during an exposure step and the effect of multiple precursor doses. This model also allowed for the optimization of the ALD modification process, including precursor usage efficiency and total process time.

SEM-EDS was used to quantify the ALD infiltration depth to validate the model. ALD saturation was further confirmed using mass gain measurements. The ALD-modified AM also showed improved resistance to structural degradation at elevated temperatures, likely due to stabilization of the SiO_2 nanoparticles. These changes may be due to the formation of a ternary Al-Si-O phase at the interface between the SiO_2 backbone and Al_2O_3-based modification, as shown using XPS measurements. This leads to an improved retention of the low thermal conductivity and high transmittance following annealing, compared to bare SiO_2 AMs. This combination of properties makes the ALD-modified AMs a promising transparent insulating material for CST applications [2]. ALD-modified AM synthesis is currently being scaled up from ~25.4 mm-diameter discs to ~155 x 65 mm tiles for use in a prototype CST receiver.

[1] A. J. Gayle, Z. J. Berquist et al. *Chem. Mater.* **2021**, *33* (14), 5572-5583.

[2] Z. J. Berquist, A. J. Gayle et al. *Adv. Func. Mater.* **2022**, 32 (12), 2108774.

11:20am **TF-TuM-11 Ultra-thin, Conformal ALD Films for Reliable Corrosion Resistance in SLM Metal Additive Manufactured Surfaces***, **Timothy J. Gorey**,* Los Alamos National Laboratory

Metal additive manufacturing (MAM) is a valuable method for prototyping and circumventing the geometry constraints of conventional manufacturing methods, such as machining or extrusion. The field of MAM is still relatively novel, and aging properties, such as unpredictable corrosion resistance, hinder widespread application and reliable interchangeability with traditionally manufactured parts. Here, we utilize the self-limiting deposition method of atomic layer deposition (ALD) to apply ultra-thin, conformal anti-corrosion barriers onto monolithic 316L stainless steel surfaces. Substantial improvement in corrosion reliability was repeatedly obtained on single-surface, proof-of-concept coupon samples for thicknesses ranging from a few to hundreds of nanometers. This presentation will discuss the unique advantages and nuances of ALD and its relevance to MAM components. Corrosion results for coated and uncoated MAM 316L surfaces will also be discussed that predict ALD to be a viable post-manufacturing approach in MAM parts.

11:40am **TF-TuM-12 Atomic Layer Deposition of Superconducting Films for Through-Silicon-Via Structures and Photon Detection***, **John Femi-Oyetoro**, H. LeDuc, P. Day, F. Greer,* Jet Propulsion Laboratory (NASA/JPL)

Superconductors traverse to normal metal behavior in the millimeter-far-IR wavelength range as consistently described in the Bardeen-Cooper-Schrieffer (BCS) theory. This property has been explored and leveraged upon in Astrophysics, for detecting the early universe in the millimeter-far-IR spectrum, where radiation appears to be the strongest. The first light emitted after the Big Bang approximately 14 billion years ago can still be detected as the cosmic microwave background (CMB), and superconductors have aided this effort. Superconducting (SC) detectors are essential and have scientific opportunities in solving key problems in astronomy and cosmology. To buttress, at Jet Propulsion Laboratory, SC transition edge sensors have been deployed at the South Pole, including the Background Imaging of Cosmic Extragalactic Polarization (BICEP) telescopes and the Keck Array. These instruments have performed CMB polarization measurements with great sensitivity to the signatures of the early universe. In addition, kinetic inductance SC detectors are been utilized in future missions and concepts such as the Terahertz Intensity Mapper (TIM) balloon experiment and Galaxy Evolution Probe (GEP) for integral field spectroscopy. In this work, we demonstrate the deposition of high-quality SC films such as titanium nitride (TiN) with high transition temperature and kinetic inductance for high-density through-silicon-via (TSV) structures for large photon detectors arrays. SC films provides outstanding sensitivity, mature fabrication, and large array sizes, for multiplexing and hybridization techniques. However, while conventional sputtering technique have been useful in fabricating SC detectors, atomic layer deposition (ALD) has provided an advantage of spatial uniformity and conformality. These properties are absent in sputtering techniques. We employed ALD to control the repeatability, composition and thickness, which plays a role in the transition temperature of SC films. These possibilities have an advantage to explore different SC materials for specific detection application in future science observations. We also explored different precursors and deposition conditions, including temperatures as low as 200 °C. In a nutshell, we are interested in TSV SC films with spatial uniformity, high-aspect-ratio and high transition temperature, that will overcome the challenges of interconnect density using 3D integration. We believe that, extending these integration techniques to SC detectors are

[1] **TFD James Harper Award Finalist**

very crucial in the 3D hybridization of high-density pixel detector arrays with outstanding sensitivity. Results aiding these TSV structures for SC detectors will be discussed.

12:00pm **TF-TuM-13 Reliable RF and DC Plasma-Power Solutions Supporting Today's Demanding Industrial Applications***, **Mike Meyer**, P. Maloney,* Advanced Energy Industries, Inc., USA

Process stability, reliability, and repeatability are key to optimizing yield in advanced plasma-based applications. As these processes become more complex, involving numerous steps and rapid plasma transitions, accurate control of the power to ignite, maintain, and manipulate the plasma becomes increasingly critical. This presentation describes developments in RF and DC power-delivery technologies and techniques that enable these demanding manufacturing applications, including bipolar DC pulsing with customizable waveforms, and RF-power phase synchronization, real-time impedance management, customizable arc management, and waveform controls. It also explains how real-time access to power-delivery data and analysis provides intelligence that engineers and operators can apply immediately to refine process performance, as well as to predict and perform maintenance. Ultimately, combining the described power hardware with these critical insights can maximize yield and minimize downtime – crucial capabilities for today's semiconductor, glass, FPD, solar, and industrial applications.

Presenters:

Mike Meyer is a senior product manager at Advanced Energy with 23 years of experience in the precision thin-film industry, including eight years with RF and DC power systems for PVD, PECVD, and a variety of industrial, plasma-based, thin-film deposition applications. He also spent 15 years in the precision optical-coating industry specializing in ion-beam sputtering technology and complete optical coating system solutions.

Paul Maloney has four years of experience in the precision thin-film industry working with Advanced Energy plasma power products. He currently leads the DC Product Management team and is developing next-generation DC and pulsed-DC power supplies. He previously worked in the defense industry and has an educational background in nuclear engineering.

Atomic Scale Processing Focus Topic
Room 317 - Session AP+PS+TF-TuA

Thermal Atomic Layer Etching

Moderators: Silvia Armini, IMEC, Belgium, **Eric A. Joseph**, IBM Research Division, T.J. Watson Research Center

2:20pm **AP+PS+TF-TuA-1 Thermal Atomic Layer Etching: The Right Etch Technology at the Right Time*, Andreas Fischer*,** *A. Routzahn, R. Gasvoda, J. Sims, T. Lill,* Lam Research Corporation **INVITED**

Thermal atomic layer etching is rapidly becoming an important complementary processing technology in manufacturing of advanced logic and memory semiconductor devices.Critically, stacked chip architectures such as 3D NAND, 3D DRAM or Gate-all-around devices require conformal isotropic etching to remove material such as HfO_2 or SiGe in hard-to-reach locations with aspect ratios that can be greater than 50:1.To achieve repeatable device performance throughout a 3D stack, the removal rate (etch per cycle) of the etched material during an etch process need to be controlled such that the overall etch is the same from top to bottom of the device stack.In this work we studied HfO_2-based 3D NAND test structures with an aspect ratio of more than 50:1. Etching was performed via ligand exchange with dimethyl-aluminum chloride (DMAC) after surfaces had been fluorinated with hydrogen fluoride (HF).Fluorination studies on blanket films revealed that fluorination efficiency is improving for pressures in the Torr range compared to previous millitorr experiments and that only temperatures above 250°C increased the fluorine concentration in HfO_2 significantly whereas fluorine levels were unchanged between 150°C and 250°C.Regarding etch rates in these 3D NAND structures, we found that the horizontal etch rate of HfO_2 as a function of depth (depth loading) depended on the DMAC dosing but was nearly independent on the HF dose.The HF dose and the process pressure were key to increasing the overall etch amount per cycle (EPC).With the highest tested HF dose of 192 Torr*s and a total process pressure of 8 Torr, we achieved a uniform etch amount of 0.6 nm per cycle.In addition, we investigated the impact of film quality and film coating conformality in these structures on the depth loading in the succeeding ALE processes.Type of precursor, precursor dosing, deposition rate as well as substrate temperature played a fundamental role in controlling the film quality and conformality of the deposited HfO_2 layers inside high aspect ratio holes.

3:00pm **AP+PS+TF-TuA-3 Atomic Layer Etching of Titanium Nitride with Surface Modification by Cl Radicals and Rapid Thermal Annealing***, N. Miyoshi,* Hitachi High Technologies America Inc., Japan*; **Nicholas McDowell**,* Hitachi High Technologies America Inc.*; H. Kobayashi,* Hitachi Global Storage Technologies Inc, Japan

Thermal atomic layer etching (ALE) is a promising method for isotropic etching with atomic level precision and high conformality over three-dimensional structures. Due to these characteristics, thermal ALE will be a crucial component of etching the next generation of semiconductor devices. In this study, a thermal ALE process for titanium nitride (TiN) films was developed using surface modification with a Cl2/Ar downstream plasma followed by infrared (IR) annealing of the films. The oxygen-free Cl2-based plasma was adopted to allow a highly selective etch with respect to various materials. Evaluations showed spontaneous etching of TiN during radical exposure can be suppressed at a surface temperature of −10 ºC. Evaluations demonstrated that this process is self-limiting with respect to both radical exposure and IR annealing. With repeated steps of self-limiting radical exposure and IR annealing, TiN was etched at 2.0 nm/cycle, while no thickness change was observed for poly-Si, SiO2, Si3N4, W, and HfO2. The selectivity of amorphous carbon was shown to be higher than 4. X-ray photoelectron spectroscopy analysis showed that the N in the TiN surface layer is spontaneously removed by Cl radical exposure as NClx and NOxCly (Due to residual O in the chamber) species and the film is left with a modified surface layer of TiClx. The remaining TiClx modified layer can then be desorbed by IR annealing, returning the surface layer to its original condition (pristine TiN).

3:20pm **AP+PS+TF-TuA-4 Thermal Atomic Layer Etching (ALE) of Metal Oxides by Chlorination and Ligand Addition using SO_2Cl_2 and Tetramethylethylenediamine (TMEDA)***, **Jonathan Partridge**, J. Murdzek, S. George,* University of Colorado Boulder

The thermal ALE of many metal oxides, such as Al_2O_3, HfO_2 and ZrO_2, can be accomplished using the fluorination and ligand-exchange mechanism.For other metal oxides, this reaction pathway is not viable because of difficulty finding appropriate ligand-exchange precursors.Fortunately, other etching mechanisms are possible based on ligand addition instead of ligand exchange.During ligand addition, the modified surface layer is volatilized by adding a ligand to the surface metal complex.This study will illustrate the ability of chlorination and ligand addition to etch a variety of first-row transition metal oxides.

Thermal ALE of Fe_2O_3, CoO, NiO and ZnO was demonstrated with sequential exposures of SO_2Cl_2 for chlorination and tetramethylethylenediamine (TMEDA) for ligand addition at 250°C.Using CoO as an example, SO_2Cl_2 chlorinates CoO to form $CoCl_2$ on the CoO surface.TMEDA then undergoes ligand addition with $CoCl_2$ surface species to form a volatile $CoCl_2$(TMEDA) etch product. X-ray reflectivity experiments measured CoO etch rates of 2-3 Å/cycle at 175 - 250°C.The volatile etch products were also identified using a new reactor equipped with a quadrupole mass spectrometer (QMS).The $CoCl_2$(TMEDA) etch product was observed by QMS analysis during TMEDA exposures.CoO etching also involves oxygen loss.Thermochemical calculations indicate that the oxygen could be lost by the formation of SO_3 or O_2.These oxygen products have not been confirmed by QMS analysis.SO_3 is unstable and difficult to observe by QMS.The cracking pattern of SO_2Cl_2 interferes with O_2 detection.

For the other metal oxides, QMS analysis observed $FeCl_2(TMEDA)^+$ ion signals for Fe_2O_3 etching during the TMEDA exposures. $NiCl_2(TMEDA)^+$ ion signals were also monitored for NiO etching during the TMEDA exposures. In addition, $ZnCl(TMEDA)^+$ ion signals were measured for ZnO etching during the TMEDA exposures.Chlorination and ligand-addition was also explored for the thermal ALE of V_2O_5, CuO, Cr_2O_3 and MnO_2. Unfortunately, V_2O_5 and CuO spontaneously etched during the SO_2Cl_2 exposure to form $VOCl_3$ and $CuCl_3$, respectively. Etch products containing TMEDA were not observed for Cr_2O_3 and MnO_2. This work illustrates that sequential exposures of SO_2Cl_2 and TMEDA will be useful for the thermal ALE of a variety of metal oxides that have stable metal chlorides and can not be etched using the fluorination and ligand-exchange mechanism.

4:20pm **AP+PS+TF-TuA-7 Thermal Atomic Layer Etch Processes in Semiconductor Manufacturing Challenges and Opportunities***, **Gert Leusink**,* TEL Technology Center, America, LLC **INVITED**

Driven by ever-increasing complexity in materials and structures, process technology requirements in semiconductor device manufacturing have evolved to control at the atomic level. In recent years, atomic level processing has been introduced in deposition, etching, and (wet) cleaning. Chemically selective and/or area-selective processes can be an efficient way to meet future manufacturing requirements[1,2]. Furthermore, damage free low temperature thermal processes will be needed to enable precise control in 3D structures with small CDs and high aspect ratios[3].

In this talk, we will review some of the fundamentals and challenges in thermal Atomic Layer Process technologies for advanced semiconductor device manufacturing. We will discuss recent trends in thermal Atomic Layer Etching (ALE) and show examples how these processes may be used to address some of the critical challenges in cleaning, etching and patterning applications in the manufacturing of 3D devices.

1. *Perspective: New process technologies required for future devices and scaling*, R. Clark [https://aip.scitation.org/author/Clark%2C+R]*et al*, APL Materials 6, (2018)
2. *Overview of atomic layer etching in the semiconductor industry,* Kanarik, K*et al,* Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films, 33(2), 020802
3. 3-D Self-aligned Stacked NMOS-on-PMOS Nanoribbon Transistors for Continued Moore’s Law Scaling, C. -Y. Huang et al, IEDM 2020

5:00pm **AP+PS+TF-TuA-9 Thermal Atomic Layer Etching (ALE) of InGaP:Processing Chemistry and Removal of Surface Defects***, **Ross Edel**, T. Nam, S. George,* University of Colorado Boulder

Thermal ALE of crystalline indium gallium phosphide (InGaP) has been developed to extend thermal ALE to phosphide semiconductor materials. These phosphide semiconductor materials are widely used as red light-emitting diode (LED) devices. Native oxides and surface defects on LED devices can lead to electron/hole pair recombination that reduces their light output. In particular, the light output can be significantly reduced on smaller devices having high surface-to-volume ratios. The surface defects

are believed to be formed by energetic ion species from previous plasma processing steps. Thermal ALE may provide a method to remove the native oxides and surface defects without causing additional damage.

This work was conducted using a new apparatus that combines a hot wall ALD/ALE reactor with *in vacuo* Auger spectroscopy. This apparatus allows the InGaP sample to be characterized throughout the thermal ALE process without exposure to atmosphere. The thermal InGaP ALE was performed using static, sequential hydrogen fluoride (HF) and dimethylaluminum chloride (DMAC) exposures. The HF/DMAC exposures were able to achieve InGaP etch rates of 0.5–1.0 Å/cycle at temperatures from 300–330 °C, respectively. The etch rates were measured for thin InGaP films on GaAs substrates using *ex situ* spectroscopic ellipsometry.

Etching with only HF/DMAC exposures could produce a chemically distinct top layer. This top layer was believed to be caused by the conversion of the InGaP native oxide to Al_2O_3 or $AlPO_4$ by DMAC. However, this conversion could be avoided by first removing the InGaP native oxide using sequential HF and trimethylaluminum (TMA) exposures. The HF/TMA exposures were able to achieve native oxide etch rates of >1 Å/cycle at temperatures above 300 °C. The underlying InGaP could then be reliably etched with no top layer formation. In the optimized process, the InGaP native oxide was first removed using sequential HF and TMA exposures. Subsequently, the InGaP was etched using sequential HF and DMAC exposures.

The removal of surface defects by ALE was also studied using *ex situ* X-ray photoelectron spectroscopy (XPS). InGaP samples damaged by Ar^+ ion sputtering were analyzed before and after thermal ALE. The XPS analysis focused on the phosphorus XPS signals that revealed the sputter damage. The proportion of the phosphorus XPS signal intensity attributed to sputter damage was found to decrease versus number of thermal ALE cycles.

5:20pm **AP+PS+TF-TuA-10 Thermal Atomic Layer Etching of MoS2 Films**, ***Jake Soares,*** Boise State University; *A. Mane,* Argonne National Laboratory; *S. Hues,* Boise State University; *J. Elam,* Argonne National Laboratory; *E. Graugnard,* Boise State University

2D materials can offer promise for a wide range of application within semiconductor manufacturing. Of these materials, molybdenum disulfide (MoS_2) is of great interest due to its high mobility, measured on/off ratio, tunable band gap, and a film thickness ideal for scaling. In order to move this material closer to integration with semiconductor manufacturing, a great amount of processing control is required. Atomic layer processing techniques can accommodate this needed precision, where both the deposition and removal of MoS_2 has been studied. In this work we report a thermal atomic layer etching (ALE) process for MoS_2 using MoF_6 and H_2O as precursor reactants. Here, we will discuss atomic layer etching of both amorphous as-deposited and crystalline MoS_2 films. In–situ quartz crystal microbalance measurements (QCM) indicate removal of as-deposited films when switching from a deposition chemistry (MoF_6 + H_2S) to the proposed etching chemistry (MoF_6 + H_2O). Saturation curves for the etching process were additionally identified with QCM by studying the mass gained per cycle versus the precursor dose duration. Films deposited on planar coupons were characterized with ellipsometry and X-ray reflectance to determine the etch per cycle. We propose the chemical reaction equations for the etch process as guided by residual gas analysis of byproduct formation, Gibbs free energy calculations, and QCM mass ratio analysis. After ALD and subsequent ALE processing, we produced few layer crystalline MoS_2 films once annealed. With the many application of both amorphous and crystalline MoS_2, this work helps to identify and expand current atomic layer processing chemistries.

5:40pm **AP+PS+TF-TuA-11 Atomically-Precise Surface Processes: From Molecular Mechanisms to Realistic Devices**, ***Andrew Teplyakov,*** University of Delaware

The atomic-level precision in designing surfaces and nanostructures is quickly making its way from the one-off laboratory investigations into chemical manufacturing. However, in order to make the applications feasible, fundamental understanding of the mechanisms of surface reactions leading to the formation of the desired surface structures is needed. A great deal of progress has been made over the years in uncovering reactions behind atomic layer deposition (ALD), but much more limited information is available about atomic layer etching (ALE), although both processes are often required to build the components of present and future microelectronics.

This talk will highlight recent work on understanding the reactions for metal and metal oxide deposition on functionalized (and patterned) surfaces and on recent advances in ALE of complex materials, specifically focused on tertiary alloys, such as CoFeB, used in magnetic tunnel junctions. I will outline the work needed to understand the mechanisms of these processes that can be further used to improve the control over atomically-precise manufacturing methods and to reduce the use of hazardous procedures. The relatively well-understood ALE procedures that include oxidation or chlorination as the first half-cycle of ALE of such materials and introduction of a bidentate ligands (such as acetylacetonates) to remove complex materials uniformly and with atomic-level control will be extended to describe the potential use of much milder conditions and reagents. A combination of experimental and computational methods will be used to make this analysis possible.

6:00pm **AP+PS+TF-TuA-12 Deposit and Etchback Approach for Ultrathin and Continuous Films Using Atomic Layer Deposition and Atomic Layer Etching**, *J. Gertsch, E. Sortino, V. Bright,* ***Steven George,*** University of Colorado Boulder

Ultrathin and continuous films are desirable in many devices such as MIM capacitors and ferroelectric tunnel junctions. Atomic layer deposition (ALD) methods are often used to deposit these ultrathin films. However, nucleation delays can lead to pinholes and thickness variations in ALD films. Higher quality ultrathin and continuous films can be obtained using a deposit and etchback approach using ALD and atomic layer etching (ALE). In this method, an ALD film is deposited to a thickness greater than the desired thickness to reduce the number of pinholes and form a more continuous ALD film. Subsequently, the ALD film is etched back to a smaller thickness using ALE.

The deposit and etchback approach can be illustrated for Al_2O_3 ALD in metal-insulator-metal (MIM) capacitors [1]. The benefit of the deposit and etchback approach can be measured by the percentage yield of MIM capacitors based on an $Ag/Al_2O_3/Al$ structure that do not have an electrical short. Al_2O_3 ALD was performed using sequential exposures of trimethylaluminum (TMA) and H_2O as the reactants. Thermal Al_2O_3 ALE was conducted using sequential exposures of HF and TMA as the reactants. The experiments confirmed that the device yield was improved using the deposition and etchback approach. For example, using device areas of 0.01 mm^2, Al_2O_3 ALD films that were grown to 5 nm in the MIM capacitor displayed a yield of 30-40%. In contrast, Al_2O_3 ALD films that were grown to 24 nm and then etched back to 5 nm to form the MIM capacitor displayed a much higher yield of 65-75%.

Additional experiments revealed that a portion of the yield improvement can be attributed to the fluorination of the Al_2O_3 ALD films [1]. Fluorination produces a volume expansion when forming AlF_3 from Al_2O_3. This volume expansion may produce a compressive stress that helps to close the pinholes. The deposit and etchback approach can also be used to improve the performance of $Hf_{0.5}Zr_{0.5}O_2$ (HZO) ferroelectric tunnel junctions. Thicker HZO films are needed to crystallize HZO films by thermal annealing. However, thinner HZO films are required for the best devices. Recent experiments have shown that the deposit and etchback approach can substantially improve the device performance of HZO ferroelectric tunnel junctions [2].

[1] J.C. Gertsch et al., "Deposit and Etchback Approach for Ultrathin Al_2O_3 Films with Low Pinhole Density Using Atomic Layer Deposition and Atomic Layer Etching", *J. Vac. Sci. Technol. A***39**, 062602 (2021).

[2] M. Hoffmann et al., "Atomic Layer Etching of Ferroelectric Hafnium Zirconium Oxide Thin Films Enables Giant Tunneling Electroresistance", *Appl. Phys. Lett.* **120**, 122901 (2022).

New Trends on Structural and Electronic Characterization of Materials, Interfaces, and Surfaces Using Synchrotron and FEL-Based Radiation Sources Focus Topic
Room 318 - Session LS2+2D+AS+TF-TuA

Role of Defects in Materials

Moderator: Takuya Masuda, National Institute for Materials Science, Japan

4:20pm **LS2+2D+AS+TF-TuA-7 Visualizing Complex Many-Body Phenomena in 2D Materials Based Heterostructures and Devices**, ***Jyoti Katoch,*** Carnegie Mellon University **INVITED**

Two-dimensional (2D) materials offer the freedom to create novel condensed matter systems, with unique properties, by mechanically assembling different (or same) 2D materials layer-by-layer to form atomically sharp vertical or lateral heterostructures. The van der Waals (vdW) heterostructures with small lattice mismatch and a relatively small twist angle between the constituent layers, have shown to exhibit

coexisting complex phases of matter including Mott insulating state, superconductivity, bound quasiparticles, and topological states. The advent of the state-of-the-art angle-resolved photoemission spectroscopy with high spatial resolution (micro- and nano-ARPES) and the ability to perform these measurements on fully functional devices, has made it possible to directly probe many exotic physical phenomena in 2D based material systems. In this talk, I will discuss the utilization of the nanoARPES to investigate the highly tunable many-body effects in 2D based heterostructures and their devices.

5:00pm **LS2+2D+AS+TF-TuA-9 Dynamic Grating Development for Neutron Imaging Across Multiple Length Scales**, ***Sarah M. Robinson***, *R. Murphy, J. LaManna, C. Wolf,* National Institute of Standards and Technology (NIST)*; Y. Kim, M. Daugherty,* National Institute of Standards and Technology (NIST)/ University of Maryland, College Park*; M. Huber, P. Bajcsy, P. Kienzle, K. Weigandt, D. Hussey, N. Klimov,* National Institute of Standards and Technology (NIST)

Current neutron scattering techniques can provide sample structural information on the length scales of nano- to micrometers, but it is challenging to investigate the hierarchical structures found in non-homogeneous samples. We are developing a far-field grating interferometer (INFER) to nondestructively study the microstructures of samples averaged over a voxel size of 50 µm. In order to perform far-field neutron interferometry across multiple length scales, a large number of source grating periods are used to multiplex the signal and impart the required transverse quasi-coherence. To eliminate the need of fabricating, installing, and aligning a new static source grating for each period, we have developed a DynAmic ReconfIgUrable Source grating (DARIUS). DARIUS is a wafer-scale silicon microfluidic device that allows for the real-time adjustment of the grating period, ranging from 20 µm to 20,000 µm, with the potential to replace more than 500 static source gratings. In DARIUS, each of 5,000+ individual grating channels can be selectively infilled with a neutron and x-ray absorbing fluid to modulate the neutrons, creating an absorbing grating with an effective period based on the locations of the opaque fluid. A key part of DARIUS is a diffraction grating layer fabricated on a 100 mm Si wafer. In this layer, the grating channels are etched in silicon with period of 20 µm and depth of 125 µm, corresponding to a channel volume of enough fluid to locally attenuate the neutron beam. We have previously demonstrated that we can selectively fill 128 active channels with x-ray absorbing solution and, with that, modulate in real time an x-ray beam. Our next prototype, DARIUS-2.0, has an active area of 40.96 mm x 51.20 mm with 2,560 active channels on a single side of a 100 mm Si wafer. The channels are sealed by wafer-scale eutectic bonding to a capping wafer with vias for well and pumping port access. We will present results on initial testing of DARIUS-2.0 with x-ray imaging and progress on scaling up to a double-sided grating device to be incorporated in INFER to unlock the ability of analysis over a wider range of length scales.

5:20pm **LS2+2D+AS+TF-TuA-10 Dynamics, Stability and History-Dependence of Magnetic Skyrmions in the 2D van der Waals Magnets Fe_xGeTe_2**, ***Kai Litzius***, *M. Birch, L. Powalla, S. Wintz,* Max Plank Institute for Intelligent Systems, Germany*; M. Weigand,* 4Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Germany*; K. Kern, M. Burghard, G. Schutz,* Max Plank Institute for Intelligent Systems, Germany **INVITED**

Recently, the combination of 2-dimensional (2D) magnetism [1] with the field of spintronics, i.e. the manipulation of magnetic states with electric currents, has started to gain much traction in modern solid-state physics. The prospect of highly efficient low-dimensional devices, extreme ease to fabricate versatile heterostructures by stacking of separate individual layers, and the report of chiral topological magnetic solitons in 2D itinerant ferromagnets have further enhanced the field's interest in this fascinating class of materials. Requirements for technological implementation, however, are generally to realize both the fabrication of nanoscale devices and to understand different potential ways to tailor the material parameters and ferromagnetic ordering temperatures [2,3] in desirable ways.

In this work, we utilize real-space imaging of the magnetic texture in thin flakes of the van der Waals magnets Fe_xGeTe_2 to determine magnetic phase diagrams of various exfoliated films with varying compositions. We furthermore realize devices for local injection of skyrmions by means of vertical nanocontacts. Our findings show besides complex, history-dependent magnetization states also that changes in the composition and crystalline structure significantly alter the magnetic behavior and may be used to tune the stability of skyrmions or other magnetic textures in these novel magnetic systems. Ultimately, the choice of composition and nucleation mechanism result in a selective stabilization of a variety of (meta-) stable magnetic configurations. Especially individual skyrmions can then be injected by targeted current pulses through a nanocontact. Our findings open novel perspectives for designing van der Waal heterostructure-based devices incorporating topological spin textures.

References:

1. Burch K. S., Mandrus, D., Park, J. G. (2018). Magnetism in two-dimensional van der Waals materials. Nature 563, 47–52.

2. May A. F. et al. (2019). Ferromagnetism Near Room Temperature in the Cleavable van der Waals Crystal Fe5GeTe2. ACS Nano 13, 4436–4442.

3. Chen H. et al. (2022) Revealing room temperature ferromagnetism in exfoliated Fe5GeTe2 flakes with quantum magnetic imaging. 2D Materials 9 025017.

Plasma Science and Technology Division
Room 305 - Session PS1+TF-TuA

Plasma Processing for Advanced Emerging Memory Technologies, Advanced Packaging and Heterogeneous Integration

Moderators: Hisataka Hayashi, KIOXIA, Japan, **Samson Odunuga**, Intel Corporation

2:20pm **PS1+TF-TuA-1 Study of Residues Formation after Ge-Rich GST Etching Using Halogen Gases**, ***Benjamin Fontaine***, STMicroelectronics, France*; C. Boixaderas,* Univ. Grenoble Alpes, CEA, Leti, France*; J. Dubois, P. Gouraud, A. Rival,* STMicroelectronics, France*; N. Posseme,* Univ. Grenoble Alpes, CEA, Leti, France

Non-volatile memories patterning is being more and more challenging with dimension reduction. Germanium-antimony-tellurium alloy (GST) has been well studied for phase-change random access memory (PCRAM) applications. Previous publications have proven the interest of using halogen plasmas to etch GST with etch rate range between 200 $nm.min^{-1}$ and 700 $nm.min^{-1}$ using HBr, CF_4 or Cl_2 chemistries. The etching results in halogen implantation in the first nanometers of the material with less modified surface and better roughness using the HBr chemistry. Despite these improvements, complementary analyses recently revealed a defectivity increase (residue formation) after etching and air exposure.

In this work, we propose to study the evolution of the surface state from the first hours of air exposure to several days after the etching using Ge-rich GST full-sheets. We compared the halogen chemistries showing residues formation in the first moments of air exposure after the etching step. Throughout a kinetic study, we showed the criticality of brief air exposures and found the optimal time required for the material protection.We observed a high level of defectivity after 24h of air exposure.

Residues are known for altering devices operation. XPS and EDS analyses revealed that important surface oxidation is present when residues appear. Complementary analyzes revealed that moisture environment has also a catalytic effect on the residue formation. Based on these results, a detailed mechanism responsible of residues formation will be presented.

Using this mechanism, in-situ Post-Etching Treatments (PETs) will be proposed in order to prevent residues formation. We will implement the best PETs on real devices to verify their effectiveness.

2:40pm **PS1+TF-TuA-2 Magnetron Plasma Sputtered $Ge_2Sb_2Se_4Te$ as a Non-Volatile Optical Switch Material**, ***Steven Vitale***, *P. Miller, P. Robinson, C. Roberts, V. Liberman,* MIT Lincoln Laboratory*; Q. Du, Y. Zhang, C. Popescu, M. Shalaginov, T. Gu,* Massachusetts Institute of Technology*; M. Kang, K. Richardson,* University of Central Florida*; C. Rios,* University of Maryland*; J. Hu,* Massachusetts Institute of Technology

Commercial technologies such as non-volatile memory, integrated photonic circuits, and compact optics are enabled by amorphous-to-crystalline transition of phase change materials (PCMs); for optical applications, the key feature of PCMs is the ability to change the optical properties (n, k) of the material by switching between a high-index crystalline phase and a low index amorphous phase. Here, we study the phase transition of an IR-transparent PCM, $Ge_2Sb_2Se_4Te$ (GSST), deposited using an AJA combinatorial magnetron plasma sputtering system. The film composition was tuned by varying the RF power to each of the Ge, Sb, Te, and $GeSe_2$ sputtering targets based on measurements from an in-situ EDX spectrometer.

Microheaters were fabricated in a fully-depleted silicon-on-insulator technology and coated with GSST. Microheater temperatures in excess of the melting point of GSST (900 K) were achieved. The small mass of the microheater allows for a quenching rate in excess of 10^7 K/s which is critical for amorphization as slower cooling causes recrystallization. The microheater chips were mounted in a Raman microscope and connected to pulsed electronics and the GSST structures was measured after amorphization or recrystallization heater pulses. The characteristic Raman peak of amorphous GSST occurs at 157 cm^{-1} and is consistent with Ge-4Se tetrahedral units. The characteristic Raman peak of crystalline GSST occurs at 120 cm^{-1} and is consistent with Ge-6Se octahedral units. The fundamental crystalline-to-amorphous transition appears to be reduction in Ge coordination from six to four, with the excess selenium atoms forming an amorphous Se-Se network. The amorphous-to-crystalline transition requires breaking the Se-Se network and increasing the Ge coordination from four to six. The measured activation energy for this transition is very close to the Se-Se bond energy and is thus consistent with the proposed mechanism. Enabled by the microsecond heater response we measured an ultrafast time-temperature-transformation diagram for GSST.

No irreversible chemical change (such as oxidation or decomposition) was observed up to 1000 crystallization-amorphization cycles. Lumerical simulations of a telecom-relevant silicon photonic switch show that the measured variation in octahedral/tetrahedral content allows for acceptable insertion loss variability but improved microheater temperature reproducibility will reduce variation in output port contrast.

3:00pm **PS1+TF-TuA-3 Phase-Change Memory Materials Processing Requirements***, **Luxherta Buzi,*** IBM Research Division, T.J. Watson Research Center*; H. Cheng,* Macronix*; M. Hopstaken,* IBM Research Division, T.J. Watson Research Center*; L. Gignac,* IBM Research, T. J. Watson Research Center*; C. Tabachnick, J. Papalia, H. Miyazoe, S. Engelmann, R. Bruce,* IBM Research Division, T.J. Watson Research Center

Switching of Phase Change Memory (PCM) material between crystalline and amorphous phase with electrical pulses and optical properties make it an important candidate for storage class memory and neuromorphic computing [1-2]. These PCM materials (e.g., GeSbTe and its derivatives) can be damaged during plasma etch processing leading to poor performance and yield [3-4]. Surface oxidation of PCM materials can substantially alter switching properties therefore, in-situ encapsulation has been viewed as a favorable solution [5]. It is imperative that RIE and encapsulation mitigate damage or oxidation of PCM material during integration. This paper reviews the effects of etch chemistry, temperature, plasma reactor, and post RIE processing on material properties [3, 6]. In-situ encapsulation of GST and tuning of plasma parameters, caused controlled SiN film deposition with simultaneous selective etching of GST [6]. We have also demonstrated that using alternative chemistry for PECVD film encapsulation can improve GST switching properties and provide a good barrier for GST oxidation.

[1] H. Tsai, et al., Journal of Physics D: Applied Physics, 51, (2018).

[2] S. Ambrogio, et al., Nature, 558, 60-67 (2018).

[3] L. Buzi, et al., SPIE 2021 doi: 10.1117/12.2581706

[4] H-Y. Cheng et al 2019 J. Phys. D: Appl. Phys. 52 473002

[5] P. Noe et al., Acta Materialia 110 (2016) 142-148

[6] L. Buzi, et al., SPIE 2022, Advanced Etch Technology and Process Integration for Nanopatterning X

3:20pm **PS1+TF-TuA-4 Exploration of Alternative Hard Mask Materials for the IBE Patterning of 50nm Pitch STT-MRAM High Density Orthogonal Pillar Array***, **Romuald Blanc**, L. Souriau, W. Devulder, S. Couet, F. Lazzarino,* IMEC, Belgium

In order to approach the bit density of dynamic random access memory (DRAM), spin-transfer torque (STT) magnetic random access memory (MRAM) requires to be scaled down to pitch 50nm and below[1,2]. To fabricate 50nm pitch STT-MRAM high density pillars, ion beam etching (IBE) is used to pattern the magnetic-tunneling junction (MTJ). This etch technique relies mainly on physical ion sputtering which does not allow high selectivity to the hard mask[3], therefore a robust material is needed to avoid excessively thick hard mask and high pillar aspect ratio.

In this talk, we present the etch rate of multiple materials deposited in 300mm production tools etched with different with ion beam etching conditions. Then we demonstrate the patterning of a hybrid hard mask composed of high-density diamond-like carbon (DLC) to increase etch selectivity and TiN which will become the STT-RAM top electrode. Finally, the interest of this hybrid DLC/TiN hard mask is evaluated for the patterning of the MTJ stack with IBE.

References:

[1] Lei Wan et al, *Fabrication and Individual Addressing of STT-MRAM Bit Array With 50 nm Full Pitch*, IEEE TRANSACTIONS ON MAGNETICS, VOL. 58, NO. 5, MAY 2022

[2] Murat Pak et al, *Orthogonal Array Pillar Process Development for High Density 4F2 Memory Cells at 40nm Pitch and Beyond*, SPIE Advanced Lithography 2022, Paper 12051-45

[3] Kuniaki Sugiura et al, *Ion Beam Etching Technology for High-Density Spin Transfer Torque Magnetic Random Access Memory*, Japanese Journal of Applied Physics 48 (2009) 08HD02

4:20pm **PS1+TF-TuA-7 Patterning Approaches for Integration of Complex Metal Alloys Towards Advanced Memory and Compute Applications***, **Shreya Kundu**, F. Lazzarino,* IMEC, Belgium **INVITED**

Increasing need of data processing from core electronic devices is instrumental in driving the innovation of high-density memories and high-performance computing in the semiconductor industry. To sustain this growth in storage and computing domains, novel material systems are being investigated exhaustively due to their promising intrinsic properties. A key challenge here is their satisfactory patterning to enable assimilation into integrated chips.

Patterning studies of complex alloy systems generally aim at finding a suitable etch chemistry which promises good feature profiles with minimal physical and chemical damage. However, when integrated with diverse electrode materials (for e.g. SiN, TiN), it becomes imperative for the patterning investigation to include an additional criterion i.e., the etching of the novel alloy or the electrode should not have an adverse morphological or structural impact on one another, as it can lead to poor electrical performance. Patterning of two types of complex material systems – chalcogenide-based films (GeSbTe, SiGeAsTe/Se) and InGaZnO (IGZO) – displaying etching attributes on opposite ends of the spectrum are discussed here. Chalcogenides find widespread application in resistive, holographic non-volatile memory, and ovonic threshold switches due to their unique electronic and optical response signatures. Therefore, these materials are often integrated with optically conductive electrodes and heat sinks within an electrical circuit[1]. As chalcogenides produce highly volatile halogen-based by-products[2], prolonged exposure to similar etchants used in conventional electrode patterning schemes can cause severe undercuts leading to feature collapse. On the other hand, IGZO, a potential candidate for high performing thin film transistors[3], can be patterned using a hydrocarbon etchant and remains unimpacted by the chemistries used for etching electrode materials[4]. However, IGZO-based residues along electrode sidewalls are common post-patterning, thereby making the devices prone to current leakage.

In this talk, an overview of challenges encountered in patterning complex materials in varied integration schemes is presented followed by a systematic discussion on etch approaches to circumvent them. The repeatability and scalability of the etching schemes are also discussed.

Acknowledgments- to IMEC's Industrial Affiliation Program, IMEC's Active Memory and TIP integration team.

References

[1]N. A. Bogoslovskiy, *et al*. Semiconductors 46, 559 (2012)

[2]Canvel, *et al*, J. Vac. Sci. Technol. A 37, 031302 (2019)

[3]S. Yamazaki, *et al*. Jpn. J. Appl. Phys. 53, 04ED18 (2014)

[4]Zheng, *et al*,Plasma Sci. Technol. 14, 10, (2012)

5:00pm **PS1+TF-TuA-9 Plasma Etch Challenges and Processing Optimization in Spin Logic Device Fabrication***, **Yann Canvel**, L. Souriau,* IMEC, Belgium

Presently, microprocessor chips rely on the networking of billions of tiny switches, commonly called transistors. These CMOS-based technologies run logic operations via the electron charge to enable data computing for the function of any digital object. In the development of next-generation logic devices, an alternative solution would be to leverage the electron's spin instead of the electron's charge. This specific electron manipulation paves the way towards the fabrication of spin logic devices which promises high performances and low power consumption.

In this communication, close attention will be dedicated to the unique patterning challenges of such architectures. It mainly consists of creating a magnetic interconnect system to propagate, in a controlled way, the

information through the magnetic logic circuit. Ion Beam Etch (IBE) technique is used to shape the magnetic track. The critical point is to control the vertical etch of the Magnetic Tunnel Junction (MTJ) stack at nanometric scale. In this frame, a deep understanding of the plasma-surface interaction is required and will be presented here. As a result, some process optimization will be discussed to mitigate the ion-induced damages. Both soft landing and cyclic IBE approaches will be highlighted as proof of concept.

Raymenants, E. *et al.* Nanoscale domain wall devices with magnetic tunnel junction read and write. *Nat Electron* **4**, 392–398 (2021).

Raymenants, E. *et al.* All-Electrical Control of Scaled Spin Logic Devices Based on Domain Wall Motion. *IEEE Trans. Electron Devices* **68**, 2116–2122 (2021).

Raymenants, E. *et al.* Magnetic domain walls: from physics to devices. in *2021 IEEE International Electron Devices Meeting (IEDM)* 32.3.1-32.3.4 (IEEE, 2021).

5:20pm **PS1+TF-TuA-10 Effects of Bias Frequency on High Aspect Ratio Etching Using Voltage Waveform Tailoring**, ***Florian Krüger,*** University of Michigan*; H. Lee, S. Nam,* Mechatronics Research, Samsung Electronics Co., Ltd., Republic of Korea*; M. Kushner,* University of Michigan

The continuing reduction of feature sizes and increasingly high aspect ratios (HAR) in plasma etching pose major challenges to high volume manufacturing of nanoscale semiconductor devices. Capacitively coupled plasmas (CCPs) are an important tool for HAR etch processes. In these systems, the DC self-bias is used as a measure of mean ion energies incident onto the wafer. DC bias is coupled to the asymmetry of the system which can be a function of geometry, material differences, magnetic configurations and the use of non-sinusoidal voltage waveform tailoring (VWT) through the electrical asymmetry effect.

We computationally investigated the consequences of bias frequency on ion energy distributions (IEDs) and SiO_2 etch properties when varying the electrical asymmetry of the bias waveform.The electrical asymmetry is controlled with the phase shift of the even harmonics ϕ of a multifrequency waveform.The system is a CCP with high frequency source power and low frequency bias power.The plasma was sustained in fluorocarbon gas mixtures at 40 mTorr. The bias waveform consisted of 5 harmonics with a base frequency of 1 to 10 MHz. The gas phase simulations were performed using the Hybrid Plasma Equipment Model (HPEM).Using reactive fluxes to the wafer from the HPEM, etching of a HAR via in SiO_2 was simulated using the Monte Carlo Feature Profile Model.The resulting features were evaluated based on etch rate, etch depth and distortion.

We found that at sufficiently high bias frequencies where ions are unable to react to time-varying fields in the sheath, IEDs are dominantly affected by time-averaged sheath electric fields. Mean ion energy is correlated to the DC self-bias, which in turn is correlated to ϕ**.** In this regime maximumion energies occur when ϕ=0, and electrical asymmetry as well as DC self-bias magnitude are maximum. The resulting etch features have most desirable qualities when ion energies are high at low phase angle.

This trend does not apply and, in fact, reverses for low bias frequencies where ions are able to dynamically react to transient electric fields. This leads to temporal variations in ion energies and fluxes which result in higher ion energies at higher phase angles and lower electrical asymmetry. The trend of reversal in ion energies with phase angle also translates to the etch feature having better overall quality at high phase angle. We conclude that when using VWT techniques for process control in etch systems, there are two frequency regimes (dynamic-ions and stationary-ions) having different control mechanisms.

Work supported by Samsung Electronics and the National Science Foundation.

5:40pm **PS1+TF-TuA-11 Wafer Bevel Deposition by Localized SiO_2 and Si_3N_4 PECVD and Application to 3D Integration**, ***Francois Boulard,*** *F. Fournel, V. Lapras, L. Brunet, D. Truffier-Boutry,* CEA-University Grenoble Alps, France*; P. Ruault,* Lam Research, France*; M. Keovisai,* Lam Research*; C. Porzier, V. Gros, N. Posseme,* CEA-University Grenoble Alps, France

As 3D integration schemes move forward new process challenges arise. One of them is to manage contamination issues of multiples stacked wafers. Particularly, wafers edge and bevel are known to be the source of delamination or defects, as metals or particles contaminations[1-3]. This is even more critical after bonding when back-end of line wafers are reprocessed on front-end tools[4]. In this paper, we present a strategy consisting in encapsulating the bevel area in a single process step. SiO_2 and Si_3N_4 are deposited by PECVD at 350°C on blanket 300mm Si and CMOS + 4 BEOL levels wafers. We study the influence of pressure, RF power, and single or dual frequency plasma excitation on deposition rate, refractive indexes, and films stoichiometries by XPS. No deposition occurs on most of the top surface since the gap between the wafer front side and the top grounded electrode remains below 1 mm. On the wafer edge and bevel, where plasma and deposition take place, films wet etch rates confirm oxide and nitride excellent qualities. The radial deposition profiles is characterized by ellipsometry and scanning electron microscopy cross section. The integration of bevel deposition on CMOS+M4 products is studied. We demonstrate the compatibility of the approach with top tier bonding and the effectiveness of the encapsulation to control BEOL metal contamination.

(1)C.Bunke, T.F. Houghton, K. Bandy, G. Stojakovic, and G. Fang,IEEE TRANSACTIONS ON SEMICONDUCTOR MANUFACTURING, VOL. 26, NO. 4, NOVEMBER 2013

(2)A.Vert, et.al., 2015 26th Annual SEMI Advanced Semiconductor Manufacturing Conference, ASMC 2015, 7164420, pp. 362-366

(3)M.C. Silvestre, et.al., 2016 27th Annual SEMI Advanced Semiconductor Manufacturing Conference, ASMC 2016, 7491136, pp. 124-128

(4)L. Brunet, et. al., Technical Digest - International Electron Devices Meeting, IEDM [https://www.scopus.com/sourceid/26142?origin=resultslist], 2018-December,8614653, pp. 7.2.1-7.2.4

6:00pm **PS1+TF-TuA-12 Plasma Etching of Copper for the Microfabrication of High-Density Interconnects in Advanced Packaging**, ***Juliano Borges,*** *M. Darnon, Y. Beilliard, D. Drouin,* Université de Sherbrooke, Canada

Low-cost and high-density redistribution layers (RDL) in integrated circuits packaging are essential to support further development in the fields of high-performance computing and internet of things. Indeed, both require low-cost electronic systems capable of delivering higher bandwidths, improved operation speeds, and enhanced power performance, which can be done by in-package multi-chiplets interconnection.

Organic or silicon interposers have been developed to allow the connection of dies in 2D configurations. Even if silicon-based interposers offer the best interconnects density, they cannot be used in high-frequency applications due to the high resistive losses induced by silicon and their cost is prohibitive for consumer electronics applications. High-density RDL fabrication on organic interposers is therefore required for high-frequency operation and low-cost manufacturing. However, conventional organic interposer fabrication methods by semi-additive processes are not compatible with high-density RDL (<2 µm pitch) because of isotropic wet etching of the seed layer. On the other hand, damascene processes cannot be performed on organic substrates because of substrate warpage. We propose to revisit copper etching processes for high-density RDL fabrication on organic substrates.

Chlorine-based plasmas have been explored as an alternative for etching copper, generally employing cyclic approaches. $CuCl_2$ species are formed upon exposure to Cl radicals and can be transformed into volatile Cu_3Cl_3 when exposed to hydrogen [1]. We developed a one-step $Ar/Cl_2/H_2$-based plasma in an inductively coupled plasma (ICP) chamber with a cathode temperature of 200°C. Using this process, we demonstrated the anisotropic plasma etching of copper with an etch rate of 500 nm/min. A specific seasoning and cleaning process was also set up to provide reproducible etching conditions with no significant chamber contamination after cleaning. By optimizing the etch process, we were able to fabricate high-density copper-based RDL with a pitch of 2 µm. Preliminary tests validated the compatibility of the process with organic substrates.

These results demonstrate the capability of plasma etching processes to etch copper for the fabrication of high-density RDL on an organic substrate for advanced packaging applications.

[1]N. S. Kulkarni and R. T. DeHoff, “Application of Volatility Diagrams for Low Temperature, Dry Etching, and Planarization of Copper,” J. Electrochem. Soc., vol. 149, no. 11, p. G620, Oct. 2002, doi: 10.1149/1.1513986.

Thin Films Division
Room 316 - Session TF2+2D-TuA
Low Dimension Material Application

Moderator: Mark Losego, Georgia Institute of Technology

2:20pm **TF2+2D-TuA-1 Operando and High-throughput Approaches to Advance Integrated Process Technology of Atomically Thin Device Materials*, Stephan Hofmann,*** University of Cambridge, UK **INVITED**

For the ever increasing family of layered 2D materials many exciting properties and device concepts have been reported, yet the understanding of fundamental mechanisms that can underpin scalable process technology for these materials is lagging far behind. We developed cross-correlative operando probing capability to "unblind" the underlying mechanisms, including open and closed cell approaches for XPS, optical spectroscopy, and scanning and transmission electron microscopy. While the previous focus has been to sample select process conditions, this talk will focus on our efforts to access and fast screen the entirety of the vast, interconnected parameter space. We report on an approach to bring together substrate preparation, specifically single crystal metal catalysts, and 2D growth in a combined process flow using a standard cold-wall CVD reactor.[1] This enables large scale data acquisition and new optimisation approaches for holistic end-to-end process development, comprising growth, handling, transfer, and heterogeneous device integration for atomically thin films, particularly for emerging (opto)electronic devices where clean interfacing is crucial. We adapted a SEM to allow operando reaction monitoring for the formation and etch reactions of atomically thin WS_2 layers. This allows us to unlock a data-driven approach to understanding the underlying complex kinetics across scales. We also explored new characterization approaches for accessing pertinent device interfaces, such as TMD heterostructures,[2] and functional defects, such as emissive defects hosted in h-BN for nanophotonics, sensors, and quantum metrology and technology.[3]

[1] Burton et al., ACS Nano 14, 13593 (2020), Burton et al., submitted (2022)

[2] Schmitt et al., Nature, Accepted (2022)

[3] Stern et al, ACS Nano 13, 4538 (2019); Stewart et al., ACS Nano 15, 13591 (2021).

3:00pm **TF2+2D-TuA-3 Versatile Synthesis of 2D Superlattices from Conversion of Sequentially Layered Sub-nanomater Metal Films*, Nicholas Glavin*[1]**, Air Force Research Laboratory, Materials and Manufacturing Directorate, USA

Manipulation of bulk material properties by controlling layer-by-layer chemistry and structure of nanomaterials has remained an overarching goal of nanoscience and nanoengineering. In the case of 2D materials, heterostructures consisting of different compositions, stacking and orientation have been demonstrated leading to possibilities of artificially stacked van der Waals materials. To date, structure tunability, scalability and control of synthesis has remained a challenge. Most attempts to overcome this limitation have relied on layer-by-layer growth or transfer of grown single layers or multi-precursor growth of few-layer structures but none of these methods have the potential of scalable synthesis of controlled, periodic 2D superlattice structures.In this talk, we discuss a method to directly convert easily fabricated sub-nm metal multi-layer heterostructures on both sapphire and SiO_2 substrates followed by conversion to scalable 2D van der Waals superlattices that exhibit novel properties compared to individual 2D layers themselves including reduced bandgap, enhanced light-matter coupling, and improved catalytic performance. By annealing wafer-scale layered molybdenum/tungsten heterostructures in chalcogen vapors between temperatures of 400-800 °C, formation of mixed and horizontally-oriented superlattices as well as horizontal and vertically oriented alloys are realized. This versatility enables tunable orientation, layer structure, and chemistry in an exciting class of 2D nanomaterials and provides an opportunity to generate a wide range of artificially stacked multi-compositional 2D superlattices in controlled morphologies.

3:20pm **TF2+2D-TuA-4 Study of the Functionality of Spin Crossover Thin Films on the Ti_3C_2 Mxene Substrates*, Saeed Yazdani*,** *J. Phillips,* Department of Physics, Indiana University-Purdue University Indianapolis; *B. Wyatt,* Department of Mechanical and Energy Engineering, and Integrated Nanosystems Development; *P. Wang, M. Shatruk,* Department of Chemistry and Biochemistry, Florida State University; *B. Anasori,* Department of Mechanical and Energy Engineering, and Integrated Nanosystems Development; *P. Dowben,* Department of Physics and Astronomy, Jorgensen Hall, University of Nebraska; *R. Cheng,* Department of Physics, Indiana University-Purdue University Indianapolis

Spin crossover (SCO) molecules are a class of complexes promising for use in molecular-based devices due to the change in conductance that accompanies the change in spin state by an external stimulus. Different substrates can drastically interact with SCO molecular thin films at the interface. Although metallic substrates due to their high conductance and other unique properties are points of interest to be used as substrates for many devices, they tend to lock the spin state of SCO molecular thin films near the interface due to the strong coupling between SCO complexes and high electron density on metallic surfaces. Both experimental measurements and theoretical studies demonstrated that two-dimensional (2D) surfaces have minimum interaction with SCO complexes. In this work, for the first time, the properties of SCO molecular thin films on conductive 2D Ti_3C_2 MXene are studied. Various techniques including atomic force microscopy (AFM), UV-Vis spectroscopy, and electronic transport studies are utilized to study the functionality of $[Co (SQ)(Cat)(3\text{-}tpp)_2]$ SCO molecules. Conductive 2D MXene with outstanding electronic, optical and mechanical properties can be considered as an alternative substrate.

4:40pm **TF2+2D-TuA-8 AVS Thin Film Division/Graduate Student Harper Award TED-Talk Competition*,***

[1] **TFD Paul Holloway Award Winner**

Plasma Science and Technology Division
Room 305 - Session PS1+AP+TF-WeM

Plasma Deposition and ALD Processes for Coatings and Thin Films

Moderators: Sumit Agarwal, Colorado School of Mines, **Adriana Creatore**, Eindhoven University of Technology, Netherlands

8:00am **PS1+AP+TF-WeM-1 Hollow Cathode Enhanced Capacitively Coupled Plasmas in Ar / N_2 / H_2 Mixtures and Implications for Plasma Enhanced ALD**, ***David Boris,*** U.S. Naval Research Laboratory; *M. Johnson,* Syntek Technologies; *C. Eddy,* ONR Global; *S. Walton,* U.S. Naval Research Laboratory

Plasma enhanced atomic layer deposition (PEALD) is a cyclic atomic layer deposition (ALD) process that incorporates plasma-generated species into one of the cycle sub-steps. The addition of plasma is advantageous as it generally provides unique gas-phase chemistries and a substantially reduced growth temperature compared to thermal approaches. However, the inclusion of plasma, coupled with the increasing variety of plasma sources used in PEALD, can make these systems challenging to understand and control. This work focuses on the use of plasma diagnostics to examine the plasma characteristics of a hollow cathode enhanced capacitively coupled (HC-CCP) plasma source, a type of plasma source that has seen increasing attention in recent years for PEALD. Ultraviolet to near-infrared (UV-NIR) spectroscopy as well as spatially resolved Langmuir probe and emissive probe measurements are employed to characterize an HC-CCP plasma source using nitrogen based gas chemistries typical of nitride PEALD processes. Spectroscopy is used to characterize the relative concentrations of important reactive and energetic neutral species generated in HC-CCP systems as a function of applied RF power, gas chemistry and pressure. In addition, the electron energy distribution function, electron temperature, plasma potential, and plasma density for the same process parameters are examined using an RF compensated Langmuir probe and emissive probe.These measurements indicated that electron temperature (T_e), electron density (n_e), and plasma potential (V_p) varied significantly over the operating conditions examined with Te varying from 1.5 to 8 eV, Vp varying from 30V to 90V, and ne varying between 10^{15} m-3 and low 10^{16} m-3.This wide range plasma conditions is mediated by a mode transition from a low T_e, high ne mode of operation at low pressure (<100 mTorr) to a high T_e, low n_e mode at higher pressures (>100 mTorr).These operational modes appear analogous to the classical γ and α modes of traditional capacitively coupled plasmas.Atomic N and H densities also vary significantly over the operating conditions examined.

8:20am **PS1+AP+TF-WeM-2 Chasing Oxygen Out of Nitrides Grown on PEALD and Thermal ALD**, ***Bangzhi Liu,*** The Pennsylvania State University; *B. Rayner,* KJ Lesker

It is not uncommon to see O content above 10% inside nitrides grown on both thermal and plasma ALD reactors. One typical example is TiN. Ti is extremely reactive and will combine with any O present inside the reactor. It has been reported that O can come from multiple sources [1], including o-ring seals, impurities inside UHP gases (Ar and N2), plasma tube, etc. By adding differential pumping to gate valve seal, chamber seal, and plasma tube seal on our Lesker 150LX system, and purifying Ar and N2 gases, the O level is reduced below 1% inside TiN film. By correlating TiN growth per cycle, ellipsometry thickness uniformity mapping, and sheet resistance to O level measured by XPS, we can monitor O level inside the reactor precisely and verify the ultra-high purity (UHP) condition of the chamber. By maintaining UHP condition, extreme high purity AlN and BN have been prepared. Surprisingly, extremely low-level O (barely detectable by XPS) was found inside ZrN prepared on our thermal ALD reactor, Lesker 150LE due to a special design of the chamber. This opens a door to high purity nitrides on thermal ALD reactor. In this talk, experimental data will be presented to show the interaction between O level inside ALD nitrides and system design.Practical engineering controls enabling UHP nitrides will be discussed.

[1] Ultrahigh purity conditions for nitride growth with low oxygen content by plasma enhanced atomic layer deposition, J. Vac. Sci. Technol. A 38, 062408 (2020); Gilbert B. Rayner, Noel O'Toole, Jeffrey Shallenberger, et al.

8:40am **PS1+AP+TF-WeM-3 Area-Selective Deposition: A Bottom-Up Approach to Nanoelectronics Fabrication**, ***Silvia Armini,*** IMEC, Belgium **INVITED**

Area-selective deposition (ASD)-driven processes recently gained a lot of attention from the microelectronics industry as a potential solution for the issues associated with top-down pattern formation at the nanoscale.

The first part of this talk is focused on the ASD of TiO_2 and Ru deposited by atomic layer deposition (ALD). In this respect, as an ALD inhibition route, we have been investigating both hydrogen and halogen plasma surface modification of amorphous carbon materials (non-growth area) and methyl-terminated monomolecular organic films on SiO_2 (non-growth area) substrates. On one side, on a-C non-growth area, we examined the possibility of combining two defect-reduction strategies by employing low power Cl_2 or CF_4 plasmas for both surface functionalization/re-functionalization and for removal of nuclei.

The second part of this talk is focused on selective metal passivation films for Dielectric on Dielectric deposition. We review our current understanding of the relationship between structure and properties of the inhibiting materials and the correspondent surface dependence of different ALD processes. Nucleation and growth behaviour of ALD on different surfaces functionalized by organic films will be analyzed, such as the interaction between ALD conditions (i.e. temperature, coreactants...) and the extent of decomposition and modification of the organic films.

9:20am **PS1+AP+TF-WeM-5 The Role of Plasma in Plasma Enhanced Atomic Layer Epitaxy**, ***Scott Walton,*** *D. Boris,* US Naval Research Laboratory; *M. Johnson,* Syntek Technologies, Inc.; *V. Wheeler, J. Woodward, S. Rosenberg, S. Johnson,* US Naval Research Laboratory; *K. Ludwig,* Boston University; *J. Hite, C. Eddy,* US Naval Research Laboratory

Plasma-enhanced atomic layer deposition (PE-ALD) is a low temperature, conformal, layer-by-layer deposition technique that is based on a pair of self-terminating and self-limiting gas-surface half-reactions, in which at least one half-reaction involves species from a plasma.This approach generally offers the benefit of substantially reduced growth temperatures and greater flexibility in tailoring the gas-phase chemistry to produce films of varying characteristics and has been successfully employed to grow epitaxial films.The plasma-based advantages come at the cost of a complex array of process variables that can drastically impact the resulting film properties.We employ plasma diagnostics to inform the choice of process conditions for PE-ALD systems including VUV-NIR spectroscopy, charged particle collectors near the substrate, and spatially resolved Langmuir probe measurements to characterize the plasma used in commercial and research PE-ALD tools.In particular, we assess the total ion flux reaching the substrate surface, spatial variation of plasma properties, and the relative fractions of atomic and molecular species generated in the plasma under a variety of pressures and gas input flow fractions typically used to grow epitaxial nitride and oxide films. Changes in plasma parameters are then linked with changes in growth modes and characteristics of films including AlN, InN, TiO_2 and Ga_2O_3. This work is partially supported by the Office of Naval Research and the Naval Research Laboratory base program.

9:40am **PS1+AP+TF-WeM-6 Plasma-Enhanced Atomic Layer Deposition of TiAlN Thin Films: A Novel Approach for MAX-phase Synthesis**, ***Moses Nnaji,*** Georgia Institute of Technology, USA; *D. Hitchcock,* Savannah River National Laboratory, USA; *E. Vogel,* Georgia Institute of Technology, USA

MAX-phases are a class of layered hexagonal carbides and nitrides that possess a hybrid metal-ceramic character with a desirable combination of mechanical properties.[1] Consequently, many MAX-phase coatings are attractive for applications requiring extreme heat and corrosion resistance. However, conventional synthesis of MAX-phases such as $Ti_{n+1}AlX_n$ requires high-temperatures (800-1000 °C), limiting applications for temperature-sensitive materials.[2] Plasma-enhanced atomic layer deposition (PEALD), however, may be capable of MAX-phase $Ti_{n+1}AlX_n$ synthesis at low temperatures (<600 °C) since it (1) uses forms of energy other than high temperature to achieve crystallization and (2) creates short elemental diffusion distances to lower the energy necessary for atomic migration and crystallization. Using gaseous precursors and plasma co-reactants, the layer-by-layer growth mode of PEALD boasts conformal deposition of various carbides and nitrides at low temperatures (150-300 °C).[3] However, PEALD has yet to be demonstrated for synthesis of MAX-phase thin films.

By characterizing the stoichiometry and crystallinity of PEALD-grown films, our work explores the viability of PEALD for synthesis of MAX-phase Ti_2AlN. In this work, tetrakis(dimethylamido)titanium (TDMAT) and trimethylaluminum (TMA) precursors with N_2/H_2 plasmas are used for

deposition of composite TiAlN films on SiO_2/Si and Al_2O_3 substrates, which are then annealed under various conditions. Our work shows that the Ti:Al ratio can be easily controlled by the TDMAT:TMA cycle ratio, while higher growth temperatures and H_2 plasma induce N-deficient TiN and Al layers for a stoichiometry closer to the composition of Ti_2AlN. Furthermore, annealing of PEALD-grown TiAlN is observed to induce desorption of Al and N, a mechanism seen in conventionally sputtered Ti/AlN composites that leads to formation of MAX-phase Ti_2AlN. The effects of contamination and as-deposited crystallinity on the final composition and structure of annealed PEALD-grown TiAlN are investigated.

[1]Barsoum, M. W. et al. (2000). *Prog. Solid. State Chem.*, *28*(1-4), 201-281.

[2]Eklund, P. et al. (2010). *Thin Solid Films*, *518*(8), 1851-1878.

[3]Profijt, H. B. et al. (2011). *J. Vac. Sci. Technol. A: Vac. Surf. Films*, *29*(5), 050801.

Acknowledgments: This work was supported by Battelle Savannah River Alliance, LLC under Contract No. 89303321CEM000080 with the U.S. Department of Energy and performed in part at the Georgia Tech Institute for Electronics and Nanotechnology, a member of the National Nanotechnology Coordinated Infrastructure, which is supported by the National Science Foundation (Grant ECCS-1542174).

11:00am **PS1+AP+TF-WeM-10 AVS Graduate Research Awardee Talk: Temporal Evolution of Densities and Temperatures in Sub-Microsecond Pulsed Microwave Discharges***, **Dhruval Patel**[1][2], T. Choi, H. Swearingen,* University of Illinois at Urbana Champaign*; D. Jacobson,* Lyten*; J. Bruehl,* University of Illinois at Urbana Champaign*; B. Gittleman, M. Stowell,* Lyten*; E. Barlaz, S. Dubowsky, D. Ruzic,* University of Illinois at Urbana Champaign

Material synthesis in plasma reactors have been long investigated as an alternative to more traditional thermochemical reactors. The promise of efficient reaction channels has extended the use of plasmas in synthesis of more exotic materials such as graphene. Ever since its discovery, tremendous effort has been put towards realizing a scalable plasma-based graphene synthesis process. However, further optimization of these reactors is still required before a commercially viable process can be achieved.

Non-thermal pulsed plasma discharges can provide a gateway to a more efficient conversion of methane, primarily due to enhancement of vibrational excitations. In such discharges, the electron, vibrational and rotational temperatures can vary over the duration of the pulse and must be accounted for to accurately describe the reaction kinetics. This work aims to obtain these temperatures along with densities of hydrogen in the methane discharge over the course of the pulses to both characterize the plasma and estimate methane cracking efficiency. We also consider the hydrogen radical density as this can be used as a proxy to understand the reactions mechanisms. To do so, time gated emission spectrums for the Ar-CH_4 plasmas are obtained and analyzed. The electron temperature is inferred from various $Ar2p_{10-1}$ – $Ar1s_{5,2}$ transitions spanning 690 nm - 815 nm. The vibrational and the rotational lines are determined by spectral fitting of C_2 swan bands or CH A^2D-^2C bands. Hydrogen densities are obtained using actinometry by using trace amounts of Kr (<0.5%). A simple model is used to deduce the approximate densities of hydrogen radicals by comparing the emission of H_b to Kr $3p_{9,8,6}$ (431.96 nm, 431.86 nm, and 427.4 nm) and H_a to Kr $2p_{3,2}$ (557.03nm and 587.09 nm). Combined, these measurements will provide valuable insight into the characteristics and breakdown efficiency of methane containing pulsed plasmas.

11:20am **PS1+AP+TF-WeM-11 In situ Atomic Layer Doping Coupled Low-temperature Epitaxial Growth of β-Ga_2O_3 Films via Plasma-enhanced ALD***, **Saidjafarzoda Ilhom**, A. Mohammad, J. Grasso,* University of Connecticut*; A. Okyay,* Stanford University*; B. Willis, N. Biyikli,* University of Connecticut

Wide bandgap (WBG) semiconductors, such as GaN and SiC make up the key components of high-power high-frequency electronic devices, such as, smart power grids, 5th generation (5G) technology, and electric transportation systems. However, production complexity and high cost of these materials make such technologies less available. Gallium oxide (Ga_2O_3) is an emerging ultra-WBG semiconductor attracting great attention due to its superior electrical properties (larger bandgap ~4.9 eV, high dielectric constant 6-8 MV/cm). Additionally, to compete against the mature WBG materials which are grown typically at 700 – 1000 °C, a substantially lower temperature deposition technique for crystalline Ga_2O_3 is of particular importance for its integration with temperature-sensitive substrates or device structures.

In this study, we report on the low-temperature deposition of crystalline Ga_2O_3 films on Si, sapphire, and glass substrates via hollow-cathode plasma-assisted ALD. Films were grown using triethylgallium (TEG) and Ar/O_2 plasma as metal precursor and oxygen co-reactant, respectively. Growth experiments have been performed at 240 °C substrate temperature and 50 W rf-power. Additionally, each unit AB-type ALD-cycle was followed by an *in situ* Ar-plasma annealing treatment, which consisted of Ar-plasma exposure for 20 seconds at 250 W rf-power. Furthermore, we have employed *in situ* atomic layer doping to n-type dope *β*-Ga_2O_3 films where tris-dimethylaminosilane (TDMAS) and tetrakis-dimethylaminotin(IV) (TDMASn) were utilized as the dopant precursors. The doping process was carried out via both supercycle (ABC-type ALD-cycle) and co-dosing methods. Both *in situ* and *ex situ* ellipsometry were employed to measure the thickness and optical properties of the films. The samples exhibited enhanced growth-per-cycle (GPC) values around 1.3 Å. X-ray diffraction (XRD) of the sample on sapphire revealed epitaxial Ga_2O_3 film signature with monoclinic *β*-phase. High-resolution transmission electron microscopy (HR-TEM) revealed the epitaxial relationship of the Ga_2O_3 layers grown on sapphire substrates. Further results from our ongoing structural and electrical characterizations will provide additional insight to overcome the challenges in achieving device quality undoped and doped *β*-Ga_2O_3 layers at low growth temperatures. Comparison of Si and Sn-doping strategies will be discussed, and if needed, ex-situ thermal annealing studies will be carried out for doping activation.

11:40am **PS1+AP+TF-WeM-12 Plasma-Polymer Coating of Li-Metal Anodes for the Improvement of Li-Ion Batteries***, **Yannik Moryson**, H. Hartmann, S. Otto,* Justus Liebig University Giessen, Germany*; X. Fang,* Technical University of Darmstadt, Germany*; M. Rohnke, J. Janek,* Justus Liebig University Giessen, Germany

The demand for batteries with higher energy densities for electro mobility and energy storage still raises the question for a working lithium metal anode in battery systems. The native passivation layer on top of Li-foils is not suited to enable stable cycling of corresponding electrochemical cells due to inhomogeneities and impurities in the layer composition. These inhomogeneities and impurities will result in locally varying current densities, which lead to dendrite growth and ultimately cell failure. Artificial protection layers are one promising option to overcome these drawbacks and enable the use of lithium anodes. Here, plasma polymer coatings are a quite promising approach.

In this study, we used a self-constructed inductively coupled radio frequency (rf) plasma reactor to clean Li-foils in a first step and after that performed plasma polymerization of 1.4 bis(trifluoromethyl)benzene to deposit a passivation layer on top of lithium metal anodes and characterized the layer with time-of-flight secondary ion mass spectrometry, x-ray photoelectron spectroscopy and scanning electron microscopy. The mechanical properties of the layer were examined by nanoindentation. The results were compared with a commercial Parylene HT polymer to verify the plasma polymerization process. Additionally, we performed $^{18}O_2$ isotopic exchange experiments to determine the diffusion coefficients of oxygen in untreated Li-foils at room temperature $D = 6.3 \pm 0.5 \cdot 10^{-20}$ cm^2/s and for oxygen in the plasma polymer at room temperature $D = 3.0 \pm 0.2 \cdot 10^{-23}$ cm^2/s, which showed the protective nature of the coating. Symmetric cell tests with the coated Li electrodes showed a stable cycling behavior for over 300 h with overpotentials below 0.1 V. The electrochemical performance was clearly improved in contrast to cells with uncoated Li.

12:00pm **PS1+AP+TF-WeM-13 Fabrication and Evaluation of Composite Thin Film Membranes for Tritium Management in Future Fusion Plants***, **Adam Job**, C. Li,* Colorado School of Mines*; T. Fuerst, C. Taylor,* Idaho National Laboratory*; J. Way, C. Wolden,* Colorado School of Mines

The hydrogen isotopes tritium and deuterium are leading fuels for use in future fusion reactors. While deuterium is relatively abundant and can distilled from seawater, tritium is a radioactive compound with a short half-life that must be continuously generated and recovered from lithium-based breeder blankets. Vanadium (V)-based membranes are a promising candidate for tritium recovery due its high hydrogen permeability, thermal stability, and neutron tolerance. However, they require application of a catalytic layer to efficiently dissociate/recombine hydrogen and maintain a clean surface. Platinum group metals (Pt, Pd) are effective catalysts but rapidly alloy with V and lose activity. We are developing nanoscale

[1] **PSTD Coburn & Winters Student Award Finalist**
[2] **AVS Graduate Research Awardee**

hydrogen-permeable intermetallic diffusion barriers deposited by techniques such as reactive sputtering and atomic layer deposition. In this presentation we describe the plasma cleaning and preparation of these foils as well as the deposition of ceramic nitrides and oxides barrier layers and catalysts layers. We developed a composite structure to efficiently evaluate the hydrogen permeability of these thin films, whose properties can be orders of magnitude different than their bulk counterparts. The performance and stability of these V-based nanocomposite hydrogen membranes was evaluated as a function of temperature and hydrogen pressure. The differences between successful and unsuccessful membranes is assessed and understood through the use of materials characterization including X-ray diffraction and compositional depth profiling using TOF-SIMS and Auger spectroscopy.

Plasma Science and Technology Division
Room 315 - Session PS2+TF-WeM

Plasma Processes of Non-Silicon Related Semiconductors for Energy-Efficient Devices in Power, Photovoltaics and Optoelectronics Applications

Moderators: Kenji Ishikawa, Nagoya University, Japan, **Steven Vitale**, MIT Lincoln Laboratory

8:00am **PS2+TF-WeM-1 Low-Damage Etching of Nitride Semiconductors Utilizing Photo-Electrochemical Reactions*, Taketomo Sato,*** Hokkaido University, Japan **INVITED**

Gallium nitride (GaN), which is a III-nitride semiconductor, has wide direct bandgap (3.4 eV), high breakdown electric field (3.3×10^6 V/cm) and high saturation electron velocity (2.7×10^7 cm/sec). On the basis of excellent optical and electrical properties, significant progress has been achieved in the GaN and III-nitride based devices, such as ultraviolet laser diodes, white light-emitting diodes, and high-frequency power transistors.

For the fabrication of GaN-based devices, the etching process is one of the key-issues because GaN is a robust material with strong chemical bonds between nitrogen and Ga showing high chemical stability. Among the various etching technique, the photoelectrochemical (PEC) etching method has a great advantage in low damage and high controllability on nitride semiconductors. The PEC etching process consists of anodic oxidation of the surface and subsequent dissolution of the oxide with a chemical treatment. Since the photo-carriers generated near the sample surface is utilized to enhance the oxidation, the etching reactions easily occur even in highly-stable nitride semiconductors. In addition to this, the electrochemical reactions proceed at room temperature and follows Faraday's law. These features allow etching of nitride semiconductors with low damage and high controllability.

In this presentation, I introduce our recent work on the PEC etching of nitride semiconductors for high-power and high-frequency device application. As an example, the PEC etching process has been optimized for recess etching of AlGaN/GaN high electron mobility transistors (HEMTs), a key device in next-generation communication systems. The etching features were drastically changed with both the light wavelength and its irradiation power. Under the optimal condition, we obtained a very slow etching-rate of 0.12 nm/min, leading to a smooth and flat surface with rms-roughness of 0.4 nm. The threshold voltage (V_{th}) of recessed-gate AlGaN/GaN HEMT was precisely controlled by the residual AlGaN thickness after the PEC etching. These features are promising to realize the high-performance HEMTs with a normally-off operation.

8:40am **PS2+TF-WeM-3 Gan Profile Understanding During the Plasma Etching of an HEMT Recessed-Gate with a Photoresist Mask*, Simon Ruel,*** CEA-LETI, France*; P. Thoueille,* Lam Research Corporation, France*; P. Pimenta-Barros, N. Posseme,* CEA-LETI, France

GaN-based high electron-mobility transistors (HEMTs) constitute the next generation of high power devices after their silicon-based counterparts, because of their higher super-conducting properties offered by a two-dimensional electron gas (2DEG) channel created at the AlGaN/GaN heterojunction. For safety and consumption considerations, a Normally-Off operating mode is desirable, and possible by patterning the transistor gate with a full recess beneath the 2DEG in order to cut physically the conduction. To maximize the final device efficiency, the gate profile as well as the Plasma Induced Damage (PID) need to be well controlled. Therefore, it seems very important to understand the plasma interactions with the GaN and the associated mechanisms responsible for the GaN profile in order to better control it.

In this paper, we propose a morphological study of the gate plasma etching. The study is firstly composed of different tests and characterizations in order to understand and identify the mechanism responsible for the GaN profile. Then, the knowledge was applied to optimize the Process of Reference (POR) towards a more vertical and uniform profile.

After having opening Barc and dielectric layers, the AlGaN/GaN partial recess is done with a Cl_2/BCl_3-based RIE plasma with a photoresist mask. An etching film of the latter step was performed to identify the gate profile formation and eventual defects. We obtained a tapered profile (~50°) due to a polymer deposition on sidewall, growing with the etching time.

The characterization of these products was performed thanks to TEM EDX. The polymer may be mainly composed of C and Cl, with some traces of Ga. The presence of metallic traces explained the non-removal of the layer by an O_2 plasma.

A parametric study allows us to identify the key parameters responsible for the passivation regime and the slope control: the ElectroStatic Chuck Temperature (ESC T°), the amount of BCl_3 in the plasma, and the DC Bias voltage. Coupled with the previous analysis, we can propose a mechanism responsible for the sidewall passivation. Three main contributors are identified: a [C-Cl] compounds redeposition coming from the resist mask erosion, non-volatile Ga-based compounds [Ga-Cl] coming from the etched GaN trench, and a B_xCl_y contribution coming from the BCl_3 dissociation in the plasma.

Finally, we compared the best process obtained to the POR : it shows a more vertical and uniform GaN profile (80°) against a tapered profile with a double-slope (52°/65°) for the reference.

9:00am **PS2+TF-WeM-4 Quantitative Characterization of Plasma-Induced Defect Creation in InP Substrates Using Conductance Analysis*, Takahiro Goya,*** Kyoto University, Japan*; Y. Kodama, Y. Zaizen, M. Fukasawa,* Sony Semiconductor Solutions Corporation, Japan*; K. Urabe, K. Eriguchi,* Kyoto University, Japan

To meet increasing demands for higher operating frequency, new material-based systems that exceed the electron mobility limit of Si have attracted attention. InP is one of the promising semiconductors implemented in the next generation devices [1]. In designing the performance, the property degradation during plasma processing—plasma-induced damage (PID) [2]—is a critical issue. However, in contrast to Si devices, there have been no quantitative evaluation technique assessing the nature of PID in InP systems. In this study, we propose a defect characterization technique for InP systems using conductance analysis. N-type InP substrates were exposed to capacitively coupled plasma with Ar gas. Exposure time and peak–to–peak voltage (V_{pp}) were varied from 3 to 30 s and 270 to 450 V, respectively. We first confirmed that the present PID forms damaged layers on Si substrates whose thicknesses were approximately 5 nm by spectroscopic ellipsometry. 5.8 nm SiO_2 films were formed by ALD for electrical analyses. SiO_2/Si structures were prepared in comparison. It was revealed that tunneling current and capacitance-voltage tests (commonly employed in Si devices) were not sufficient to evaluate PID in InP systems. We applied a conductance technique [3] with an optimized equivalent circuit model. An AC modulation bias with a frequency (f_{mod}) from 100 Hz to 1 MHz was superimposed on a DC bias (V_{bias}). The peaks in conductance spectra for the SiO_2/InP devices were found to be "pinned" around 1 kHz after plasma exposure regardless of V_{bias} in depletion, whereas the peak shift in response to V_{bias} was observed for the SiO_2/Si devices. Moreover, the peak intensity for the SiO_2/InP devices increased with V_{pp}, while exposure time did not significantly impact strongly, presumably due to the dose dependence of the profile. These findings indicate that the nature of PID in InP substrates is unique, *i.e.*, the electrical response of created defects is different from that in Si devices. In addition, the PID can be quantified with the conductance method in terms of the peak intensity at a specific f_{mod}. The proposed conductance analysis is extremely useful for the PID assessment in future InP-based devices.

[1] W. R. Deal *et al.*, IEEE IEDM, 2016, p. 707.

[2] K. Eriguchi, J. Phys. D: Appl. Phys. **50**, 333001 (2017).

[3] T. Kuyama *et al.*, Jpn. J. Appl. Phys. **59**, SJJC02 (2020).

9:20am **PS2+TF-WeM-5 Impact of Bias Power and Oxygen Addition on Selective Dry Etching of TiAlC over TiN Using N_2/H_2-based Plasmas**

***Kenji Ishikawa**, T. Nguyen,* Nagoya University, Japan*; K. Shinoda, H. Hamamura,* Hitachi, Japan*; K. Maeda, K. Yokogawa, M. Izawa,* Hitachi High Technologies, Japan*; M. Hori,* Nagoya University, Japan

In the isotropic etching of multiple metal gate materials made of titanium compounds, selectivity of TiAlC against the other materials, involving metal compounds, insulators, and semiconductors, such as TiN, TaN, HfO_2, and C hard mask is required. Wet etching of Ti compounds using H_2O_2 mixtures has been conventional applied. However, this causes damage to the other exposed materials due to low etch rates and insufficient selectivity, as a result of a prolonged treatment time. To increase selectivity of etch rates for TiAlC films, the dry etching for ternary material TiAlC has been developed by processing with high density of radicals generated in a NH_4OH vapor plasma at medium-pressure plasma in our previous study [1]. This is feasible to show a potential of isotropic etching using chemistries containing NH and H.

In this study, selective dry etching of the ternary material TiAlC over TiN has been first developed using N_2/H_2-based plasmas generated from a capacitively coupled plasma etcher at low pressure. Using an *in situ* ellipsometry and an optical emission spectrometer (OES), highly selective etching of TiAlC over TiN has been investigated. In particular, addition of a small amount of O_2 (10%) into the N_2/H_2 plasmas enhanced the selectivity. A process window for selective removal of TiAlC over TiN is presented here at various bias powers, in which chemical etching was dominant at lower bias power with higher selectivity (>5). By using various mixtures of N_2, H_2, and O_2 gases for generating plasmas, surface reactions under energetic ion bombardments produces selective surface modification of the TiAlC and TiN films. Controlling O_2 addition and ion energy is essential for enabling applications of both selective anisotropic or isotropic etching of metal carbides, metal nitrides, or metal oxides.

11:00am **PS2+TF-WeM-10 Bulk Titanium Micromachining and Simultaneous Sidewalls Passivation for Bio-MEMS Applications**

***Rim Ettouri**, T. Tillocher, P. Lefaucheux,* GREMI CNRS/Université d'Orléans, France*; B. Boutaud, J. Phung, H. Philippe,* MISTIC, France*; R. Dussart,* GREMI CNRS/Université d'Orléans, France

The biomedical field has seen significant expansion because of the rise of microsystems. Even though silicon has historically been the material of choice, improvements in Titanium (Ti) micromachining have enabled the creation of bulk Ti-based devices. Whilst wet etching methods for Ti are available, they are isotropic and so restrict the geometry of features that may be created, especially at the microscopic scale. Conversely, Reactive Ion Etching (RIE) of titanium has allowed the formation of anisotropic profiles and the fabrication of biodevices such as vascular stents and micro-needles for drug delivery. In the literature, three distinct plasma chemistries for titanium dry etching have been reported with promising results: fluorinated, chlorinated, as well as combined chloro-fluorinated plasmas [1].

A method for simultaneous etching and sidewall passivation of bulk titanium is presented, which bypasses the conventional cyclic methods requiring separate passivation steps, such as the MARIO process [2]. Fundamentally enabled by the use of a continuous plasma of $SF_6/O_2/Ar$, the key novelty of this technique lies in the formation of a passivating oxide layer during micromachining . Iridescent oxide colors at the bottom of the etched Ti trenches were obtained, which result from the interference of light reflected from thin transparent oxides. Herein, we explain the oxidation mechanism that occurs during micromachining. Understanding the passivation schemes of Ti RIE is important for increasing feature aspect ratios and further miniaturization of the devices.

By adjusting the plasma parameters, the process can be controlled to achieve the best results in terms of etch rate and anisotropy while maintaining an acceptable undercut. The sidewall passivation material which is formed is found to be a titanium dioxide which contains only minor amounts of fluorine, giving the X-Ray Diffraction (XRD) patterns characteristic of rutile and anatase phases and as shown by the Energy Dispersive X-Ray Spectroscopy microanalyses (EDS). Fundamentally, the corresponding etching profiles strongly correlate the competitive effects based on the simultaneous etching and oxidation of the surface by atomic F and O, respectively.

While an almost infinite number of techniques have been used to form rutile titanium dioxide on any surface, this is yet the first time it has been reported to be achieved by RIE. This can lead to a significant increase in the potential of titanium bio-MEMS and even widen the field of application.

[1] F. Fracassi, R. d'Agostino, Pure and Applied Chemistry 64 (1992) 703-707.

[2] M.F. Aimi et al., Nature Materials 3 (2004) 103-105.

11:20am **PS2+TF-WeM-11 Selective Dry Etching of TiAlC over TiN using N_2/H_2 Plasma Chemistry**

Thi-Thuy-Nga Nguyen, Nagoya University, Japan*; K. Shinoda, H. Hamamura,* Hitachi, Japan*; K. Maeda, K. Yokogawa, M. Izawa,* Hitachi High-Tech, Japan , Japan*; K. Ishikawa, M. Hori,* Nagoya University, Japan

Selective etching of metal gate materials such as TiAlC over TiN is required in advanced fabrication of fin-type or nanosheet field effect transistor (FET) of logic semiconductor devices. The conventionally wet etching of TiAlC and TiN films using H_2O_2 mixtures causes poor etching performance and device damage. In contrast, dry etching shows advantages in controlling etchant species and their energies for both isotropic and anisotropic processes. In order to obtain higher selectivity between Ti compounds, a non-halogen chemistry for highly selective and controllable dry etching of TiAlC over TiN was reported in our previous study, which developed a feasible dry etching method for ternary material TiAlC using a high-density plasma at medium pressure [1]. For the semiconductor application, in this study, low-pressure dry etching of the ternary material TiAlC has been first developed by using N_2/H_2 plasma.

A capacitively coupled plasma etcher was used to generate N_2/H_2 plasmas, and the upper and lower electrodes were operated with 100 MHz and 2 MHz sources, respectively. Optical emission of an NH molecular line at 336.3 nm from N_2/H_2 plasmas was detected by an optical emission spectrometer (OES). The N_2/H_2 plasma can produce etchant species including NH, N, and H to form volatile products. The etch rate of TiAlC was around 2 nm/min for the N_2/H_2 plasma, whereas no etching occurred with only N_2 plasma or H_2 plasma. Selective etching of TiAlC to TiN has been successfully demonstrated.

The influence of substrate temperature on etch rate and selective etching of TiAlC over TiN was investigated in a range of -20^oC to 50^oC. The surface modification of the TiAlC and TiN films after plasma exposure was analyzed by X-ray photoelectron spectroscopy (XPS). The XPS analysis revealed that the modified layer that included N-H and C-N bonds formed only on TiAlC and not on TiN. This non-halogen plasmas etchingmethod can be applied for highly selective etching of metal carbides, nitrides, or oxides, based on proposed mechanisms for selective etching of TiAlC over TiN.

[1] T.T.N. Nguyen et al., AVS67, PS-Contributed On Demand-10 (2021).

11:40am **PS2+TF-WeM-12 Surface Modification of CoSi through Interconnect Fabrication Processes**

***Nathan Marchack**, A. Orefice, M. Hopstaken, G. Cohen, C. Lavoie, R. Bruce, C. Chen,* IBM Research

The introduction of copper BEOL interconnects played a critical role in downscaling CMOS technologies. However, at the dimensions required for future technology nodes, this mainstay faces its own set of scaling challenges, such as liner thickness limits and grain boundary scattering. [1] Topological semi-metals possess unique physical properties that make them promising candidates for the next generation of interconnect materials: namely, their resistance-area (RA) product decreases with decreasing thickness. One such material, CoSi is particularly attractive due to its compatibility with existing CMOS integration schemes. [2]

In order to facilitate patterning of semi-metals at competitive node dimensions, it is essential to investigate the influence of fabrication processes (e.g. plasma etching) on the bulk and surface properties. [3] We present surface analysis of subtractive halogen-based plasma etching of CoSi films, including effects on film stoichiometry characterized by XPS. Downstream plasma and wet solution treatments for removal of the damaged surface layers are also presented. It was found that a cyclic approach, comprising alternating exposures of inductively coupled HBr and microwave downstream H_2 plasma, provides the best stoichiometric retention. Finally, the impact of different deposition methods to form CoSi is discussed, with particular focus on the grain size disparities observed.

[1] C.-L. Lo et al., J. App. Phys. 128, 080903, 2020.

[2] C.-T. Chen et al., IEEE Int. Electr. Dev. Meeting, San Francisco, CA, Dec 12-18th, 2020.

[3] N. Marchack et al., J. App. Phys. 130, 080901, 2021.

12:00pm **PS2+TF-WeM-13 PbS Quantum Dots Thin Film Dry Etching**, ***Nicolas Le Brun,*** LTM - MINATEC - CEA/LETI, France; *P. Gouraud,* STMicroelectronics, France; *G. Cunge,* LTM - MINATEC - CEA/LETI, France; *L. Parmigiani, S. Allegret-Maret,* STMicroelectronics, France

Nowadays there is an increasing demand to enhance the capabilities of industrial products to sense their environment more efficiently, i.e. under difficult conditions (smoke, darkness…). This challenges semiconductor manufacturers because applications concern many daily life products using image sensors (smartphones, cars, automated tools…etc).

One solution studied recently is to extend the capabilities of image sensors to detect light towards the near Infrared (NIR) and Short-wave Infrared (SWIR) regions . Silicon having weak absorption properties at these wavelengths, manufacturers are looking to develop new materials which could be efficient sensors for these specific regions of the light spectrum.

To this end, quantum dot thin films are promising materials for their tunable band gap, their absorption properties, and their large-scale production availableness.

This study is related to the elaboration of sensors using PbS quantum dot thin films, and will focus on its patterning through a dry etching step. We propose to compare different etch chemistry combinations to define the best etch condition to pattern our PbS quantum dot thin films. In order to ensure the best optical properties of our material, it is crucial to control the slope of the etched profile and to prevent the uncontrolled diffusion of etchant in the quantum dot thin film stack. We will therefore monitor these key parameters under various plasma chemistry combinations as well as other dry etching settings, such as temperature or pressure.

Thin Films Division
Room 317 - Session TF1+SE-WeM

Vapor Deposition and Vapor Infiltration of Organic, Polymeric, and/or Hybrid Materials

Moderator: Siamak Nejati, University of Nebraska-Lincoln

8:00am **TF1+SE-WeM-1 Thermophysical Properties of Organic-Inorganic Hybrid Thin Films Created via Vapor Phase Infiltration (VPI)**, ***Mark Losego,*** Georgia Institute of Technology

This talk will discuss how thermophysical properties, including the glass transition, thermal expansion, and onset of crystallization, are altered when an organic material is transformed into an organic-inorganic hybrid material via vapor phase infiltration. Vapor phase infiltration (VPI) is a gas-phase technique that exposes organic materials to inorganic vapors (e.g., metalorganics or metal halides) that sorb into the organic, transforming it into an organic-inorganic hybrid. Over the past several years, our lab has examined how the precursor-organic chemistry and VPI process conditions (e.g., temperature) can be used to alter the quantity of inorganic loading and the extent to which the inorganic becomes chemically bound to the organic components. Controlling this physicochemical structure also alters the thermophysical properties of the resultant hybrid material. This talk will describe several examples including altering the glass transition temperature in poly(styrene-co-2-hydroxyethyl methacrylate) (PS-r-PHEMA) random copolymers infiltrated with aluminum oxyhydroxide and in Spiro-OMeTAD hole transport layers infiltrated with titanium oxide. In the PS-r-PHEMA system, random copolymers of varying HEMA composition from 0 to 20 mol% were investigated and the T_g was found to systematically increase with increasing HEMA temperature by as much as 40 °C. Changes in T_{-g} at low HEMA composition, for which the polymer is fully infiltrated, fit the Fox-Flory model for crosslinking phenomena which, in addition to a dissolution study on these materials, suggests that VPI crosslinks the PS-r-PHEMA, raising its glass transition temperature. Interestingly, according to the Fox-Flory model, these cross-links are 5x to 10x stiffer than usually observed for most organic crosslinks, suggesting an interesting phenomenon for inorganic cross-linking. For the Spiro-OMeTAD system, T_g appears to decrease with inorganic infiltration. This result is attributed to a lack of primary bonding between the inorganic and organic phases; the inorganic clusters now serve to disrupt the natural π-π stacking in the Spiro-OMeTAD, lowering T_g. Conversely, though, this disruption of the intermolecular forces leads to an increased resistance to crystallization in these hybrid films. This reduced propensity for crystallization may be useful for improving long-term stability of Spiro-OMeTAD-based organic electronic devices.

8:20am **TF1+SE-WeM-2 Chemical Vapor Deposition of Soft Materials for Garment-Integrated Sensor Systems and Plant Electronics**, ***Trisha L. Andrew,*** University of Massachusetts Amherst **INVITED**

Chemical vapor deposition is a single-step processing method for forming functional polymer films on unconventional substrates, such as commodity textiles and living plants, and allows fabrication of rugged and sensitive fabric-, fiber- and/or plant-based sensors for wearable electronics and smart farms. I will the detail the materials science and engineering advances made by my team during the process of assembling various garment-integrated sensor systems and plant-based sensors for longitudinal health monitoring in native environments. In particular, I will highlight our recent work in developing garments for portable brain activity monitoring and activity tracking, systems for in-home sleep monitoring, and conductive living plants for detection of selected abiotic stressors in commercial farms.

9:00am **TF1+SE-WeM-4 Effects of Trimethylaluminum Vapor Pressure and Exposure Time on Inorganic Loading in Vapor Phase Infiltrated PIM-1 Polymer Membranes**, ***Benjamin Jean,*** *Y. Ren, E. McGuinness, R. Lively, M. Losego,* Georgia Institute of Technology

Vapor phase infiltration (VPI) is a process for synthesizing organic-inorganic hybrid materials by infiltrating polymers with inorganic vapor molecules. Recently, our research team has used VPI to synthesize hybrid membranes with consistent nanofiltration performance in a variety of organic solvents that would otherwise swell or dissolve the parent polymer membrane. The properties of these hybrid materials can vary with the amount of VPI generated inorganic loading. However, the relationship between VPI processing conditions and inorganic loading is still not fully understood. This talk will discuss the effects of VPI dose pressure and exposure time on inorganic loading using the technologically relevant membrane material polymer of intrinsic microporosity 1 (PIM-1). At sufficiently low dose pressures and infiltration times (i.e., before saturation), inorganic loading can be controlled with both vapor pressure and exposure time. However, inorganic loading appears to saturate for this system at around 13 wt% inorganic. This apparent saturation point can be reached by infiltrating for 5 hours at TMA dose pressures above 0.4 Torr or after 40 hours at lower vapor pressures of 0.1 Torr. Inorganic loading appears to saturate for this system when the polymer's functional groups become fully populated with bound VPI precursors. These experimental results can be understood with the use of a recently developed reaction-diffusion model for VPI. Critical to applying this model to these post-deposition measurements is re-normalizing the mass loading to the total number of functional groups in the polymer. These findings suggest that the vapor pressure during infiltration affects the kinetics of this infiltration process but does not appear to alter the thermodynamically determined saturation point for inorganic loading.

9:20am **TF1+SE-WeM-5 Elucidating the Sequential Infiltration of Trimethylaluminum and Water Into Polycarbonate Membranes and Thin Films**, ***Rajesh Pathak,*** *R. Shevate, A. Mane , J. Elam,* Argonne National Laboratory, USA

Sequential infiltration synthesis (SIS) enables the creation of inorganic or polymer-inorganic hybrid nanocomposite materials through the diffusion of metal-organic vapor reagents into polymers and subsequent reactions with the polymer functional groups. Here we report a detailed study of aluminum oxide (Al_2O_3) SIS using trimethyl aluminum (TMA) and H_2O in polycarbonate (PC) thin films and membranes. We employed in situ Fourier transform infrared spectroscopy (FTIR) to elucidate the chemical interactions and in situ spectroscopic ellipsometry (SE) to measure the physical and optical changes that occur during Al_2O_3 SIS in PC. During the first SIS cycle, FTIR measurements revealed a rapid and irreversible reaction between TMA and the PC carbonyl groups to form Al-CH_3 species which then converted to Al_2O_3 upon H_2O exposure during.Virtually no spectral changes were observed by FTIR in subsequent SIS cycles.The SE measurements showed that the PC film thickness increased by ~75% and the refractive index (RI) decreased by ~2% during the initial TMA exposure.These effects were partially reversed during the following H_2O exposure such that the net thickness increase was ~36% and the RI returned to its initial value.During subsequent SIS cycles, the thickness and RI remained essentially constant.Ex situ X-ray photoelectron spectroscopy (XPS) depth profiling measurements showed ~30 at% Al uniformly distributed through the depth of the PC film following a single Al_2O_3 SIS cycle. SIS-derived nano/microstructure materials with tunable structural and optoelectronic properties could be developed for a variety of applications.

Keywords: atomic layer deposition; sequential infiltration synthesis; aluminum oxide, polymer-inorganic nanocomposite.

9:40am **TF1+SE-WeM-6 Kinetics of $TiCl_4$ Vapor Phase Infiltration (VPI) into PMMA and the Resulting Thermophysical and Optical Properties of the TiO_2 -PMMA Hybrids**, ***Shuaib Balogun,*** Georgia Institute of Technology*; A. Steiner,* Sandia National Lab*; M. Losego,* Georgia Institute of Technology

Vapor phase infiltration (VPI) is a post-polymerization modification technique that imbues inorganic materials into polymers to create organic-inorganic hybrid materials with new properties distinct from the parent polymer. While several VPI precursor-polymer chemistries have been explored, a lack of chemical intuition remains for fully understanding the thermodynamics and kinetics that govern the VPI process. This study seeks to continue to build this knowledge by examining the VPI process kinetics for TiO_2 infiltration into PMMA via the use of $TiCl_4$ and H_2O precursors. In this research, polymethylmethacrylate / TiO_2 hybrid materials are prepared using VPI. The depth of infiltration of the TiO_2species into ~200 nm PMMA thin films is studied using x-ray photoelectron spectroscopy (XPS), Fourier-transform infrared (FTIR) spectroscopy and spectroscopic ellipsometry. The kinetics for TiCl4 infiltration increases with both VPI process temperature and $TiCl_4$ exposure time. However, the rates of infiltration are considerably slower than those observed in the more commonly studied trimethylaluminum (TMA) / PMMA system. Even at 150 °C, process times of at least 12 hours are required to fully infiltrate a 200 nm PMMA film whereas using TMA similar films are fully infiltrated within 1 hour at the same process temperature. Films that we believe to be fully infiltrated at 150 °C and 24 hours of $TiCl_4$ exposure have a 6 at% Ti in the innermost bulk, as determined by XPS. Interestingly, unlike AlO_x-PMMA hybrids, these TiO_x – PMMA hybrids exhibit significant changes in their optical properties. Increased titanium loading leads to a 4% increase in refractive index and increased UV absorbance in the UV range of 270-350nm. Furthermore, films infiltrated at 150 °C and 24 hours of $TiCl_4$ exposure had a 50 % and 70 % reduction in coefficients of thermal expansion (CTE) below and above T_g respectively. Reduced CTE trends with increased titanium loading. We will discuss possible opportunities to use these new properties for various applications.

This project is supported by the Laboratory Directed Research and Development program at Sandia National Laboratories, a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia LLC, a wholly owned subsidiary of Honeywell International Inc. for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

11:20am **TF1+SE-WeM-11 Effect of the Metal-Heteroatom Bond on Film Growth and Properties in Vapor-Deposited, Hybrid Metal Organic Thin Films**, ***Jacqueline Lewis****, J. Shi, A. Ravi, S. I-Cheng Hsu, S. Bent,* Stanford University

Growing energy demand and the transition to clean energy set the stage for novel materials to fill gaps in current technologies. Hybrid metal organic thin films allow useful, active materials in the energy field, such as Al2O3 and ZnS, to reach a wider range of functionality by adding organic linkers via molecular layer deposition (MLD). Varying the organic linker and metal center using MLD modifies the film properties significantly, giving an adaptable, layer-by-layer growth scheme for the formation of novel materials. Previous literature reports have mainly focused on metal alkoxide films, where the organic linker is a multifunctional organic alcohol. Typically using a bifunctional linker, these films degrade rapidly in air, limiting their potential applicability for membrane materials, catalysis, and encapsulation. However, different functional groups, including dithiols, change the film properties substantially, with stability in air as one of the most notable effects. In this work, zinc thiolate films were deposited via hybrid MLD with a thiol bonding group, showing increased air stability as the films retain ~60% of the thiolate character after over 6 weeks in air. Films grown using 1,2-ethanedithiol degrade faster than those grown with 1,4-butanedithiol. The degradation mechanism forms at least three separate species, which we study via X-ray photoelectron spectroscopy (XPS) and synchtrotron-based X-ray absorption spectroscopy (XAS). Despite some degradation observed via XPS, the band gap of the material stays consistently close to 5.0 eV assuming direct band gap. This multi-week decay is much slower than the degradation of the known metal alkoxides, which degrade on the timescale of hours or days. The increased functionality exhibited by these metal thiolate films shows that changing the metal-heteroatom bond can create more stable films as well as increase the domain of materials to examine.

11:40am **TF1+SE-WeM-12 Oxidative Molecular Layer Deposition of Electrochemically Active Polymers***,* ***Matthias Young***[1]*, Q. Wyatt, M. Vaninger, N. Paranamana, T. Heitmann, H. Kaiser,* University of Missouri

Conjugated polymers such as polyethylenedioxythiophene (pEDOT), polypyrrole (pPy), and polyaniline (pAni) exhibit high electrochemical capacities, making them appealing as electrode materials for energy storage, electrochemical desalination, and chemical sensing. Recent work has established the growth of thin-films of pEDOT using alternating gas-phase exposures of EDOT monomers and a metal-chloride (e.g. $MoCl_5$) oxidant in a process termed oxidative molecular layer deposition (oMLD). Here, we report on recent work establishing oMLD of amine-containing conjugated polymers. We find that pyrrole (Py) and $MoCl_5$ undergo self-limiting surface reactions during oMLD exposures to form conformal pPy thin films, but oMLD using aniline (Ani) and p-phenylenediamine (PDA) monomers yield unexpected azo functionality. The formation of azo groups is attributed to an $MoCl_5$-amine surface adduct that spatially constrains polymerization reactions near the amine group and produces azo groups when coupling two primary amines. pPy grown by oMLD exhibits a record-breaking 282 mAh/g capacity in aqueous electrolyte, and PDA/$MoCl_5$ oMLD yields azo-polymers of interest as anode materials for alkali-ion batteries. Alternating between Py and PDA monomers during oMLD produces molecularly mixed copolymers with qualitatively different electrochemical responses from the isolated monomer structures. This work lays the foundation for the growth of conformal thin films of conjugated amine polymers with molecular-level control of composition and thickness.

12:00pm **TF1+SE-WeM-13 Towards High Throughput Molecular Layer Deposition of Alucone Films**, ***Hardik Shantilal Jain***[2]*,* Holst Centre / TNO and Eindhoven University of Technology, The Netherlands*; M. Creatore,* Eindhoven University of Technology, The Netherlands*; P. Poodt,* Holst Centre / TNO and Eindhoven University of Technology, The Netherlands

The deposition rate and properties of MLD films are for a large part determined by what happens during the precursor exposure step. In some cases, however, the purge step is of equal importance, for example in the MLD of alucone films using trimethylaluminum (TMA) and ethylene glycol (EG). Due to the porosity of alucone films, the reactants during their exposure step not only react at the film surface but also tend to infiltrate into the film. The subsequent outgassing of the infiltrated reactant can take relatively very long thereby becoming the deposition rate-limiting step. If enough purge time is not provided for the reactant to outgas, it will lead to an additional CVD component alongside MLD in the overall growth. To employ/avoid the CVD component in the deposition process, we have developed a kinetic model to correlate parameters like exposure times, partial pressures, purge times and deposition temperature to the amount of CVD component in the growth. We have also investigated the impact of this additional CVD component on the step coverage of the alucone films and evaluated its usage in superconformally filling dielectric gaps.

Additionally, we also looked into solutions to increase the deposition rate of the alucone films and improve their conformality and amongst others found that using a bulkier precursor like DMAI instead of TMA can overcome the problem of precursor infiltration, increase the deposition rate of alucone processes by at least an order of magnitude and provide quite conformal films. We also performed a detailed investigation of MLD of alucone using DMAI as the aluminum precursor wherein the effect of deposition temperature and reactant purge times on deposition kinetics has been investigated and the DMAI alucone films have been compared with those prepared using TMA for their chemical environment and degradation showing striking similarities between both. We believe that the above work could be extended to other MLD systems and can serve as a guide in designing efficient MLD reactors and processes.

---

[1] **2020 TFD Paul Holloway Awardee**

[2] **TFD James Harper Award Finalist**

Thin Films Division
Room 316 - Session TF2+AP+SE+SS-WeM
ALD and CVD: Surface Reactions, Mechanisms and Kinetics
Moderator: Jessica Kachian, Intel Corporation

8:00am **TF2+AP+SE+SS-WeM-1 Nucleation Enhancement of Ruthenium Atomic Layer Deposition Using Organometallic Molecules***, **Amnon Rothman**, D. Tsousis, S. Bent,* Stanford University

Atomic layer deposition (ALD) is an attractive surface-sensitive thin-film deposition technique used in advanced technologies such as microelectronics, catalysis, and energy applications. The self-limiting surface reactions during the ALD process promote the layer-by-layer growth mechanism, thus providing significant control over the film thickness and conformality. However, due to an island growth mechanism and nanoparticle formation, metal ALD on oxide surfaces can lead to poor-qualify films and display long nucleation delays. One of the main reasons for the nucleation delays can be attributed to the differences in the surface energy between metals and oxide surfaces. In this work, we study the nucleation enhancement of ALD ruthenium layers on Si substrates by using a single monolayer of trimethylaluminum (TMA) or diethylzinc (DEZ) preadsorbed on the substrate prior to deposition. The nucleation enhancement is demonstrated for ruthenium ALD using two different ALD precursors, cyclopentadienylethyl(dicarbonyl)ruthenium(II) (RuCpEt(CO)2) and bis(cyclopentadienyl)ruthenium(II) (RuCp2), with O2 as a counter reactant. The ruthenium ALD nucleation and growth mechanism were studied using scanning electron microscopy (SEM), ellipsometry and X-ray photoelectron spectroscopy (XPS), both on the treated and untreated substrates. The results show that pretreatments using organometallic molecules reduce the nucleation delay of the ruthenium layer. The surface pretreatment strongly influences the ruthenium nucleation, yielding up to a 1.5-fold and a 2.1-fold increase in the surface coverage of the metal while using RuCpEt(CO)2 and RuCp2, respectively. Interestingly, pulsing TMA or DEZ, with or without exposure to H2O, is equally effective. We hypothesize that the high coverage in the pretreated samples is attributed to an increase in the substrate's surface energy, enhancing the surface diffusion of nanoparticles and adatoms during growth. We confirm that exposure of organometallic molecules during ruthenium ALD using the precursors above introduces a potential pathway toward achieving high-quality ruthenium thin films.

8:20am **TF2+AP+SE+SS-WeM-2 Ald of Chalcogenide and III-V Materials for Memory Applications***, **Laura Nyns**, A. Delabie, W. Devulder,* IMEC, Belgium*; J. Girard,* Air Liquide, France*; B. McKeown, V. Pallem,* Air Liquide*; T. Peisser, J. Sinha,* IMEC, Belgium*; N. Stafford,* Air Liquide*; J. Swerts,* IMEC, Belgium **INVITED**

To enable fast and powerful storage solutions for next generation mobile applications and other innovative technologies, the memory landscape focuses on various concepts. These concepts include DRAM for high-speed access, NAND flash memory for storage of large amounts of data, and the emerging Storage Class Memories (SCM) for massive data access in short time. Each of these technologies require their own set of materials with specific characteristics. Additionally, material deposition can be challenging because of the high aspect ratios which are typical for these advanced 3D architectures. Atomic Layer Deposition (ALD) has been shown to be a promising technique in that respect, as conformal deposition of a wide range of materials in complex topographies was established over the past decades. In this talk, we will address the ALD of germanium chalcogenides, a class of materials which is being explored as phase change memory and selector elements for SCM applications. GaAs will also be discussed, due to the need for high mobility channel materials to replace poly-Si in NAND flash technologies. We used the dechlorosilylation chemistry for the ALD of chalcogenide and III-V materials, where (nonmetal) alkylsilyl compounds react with metal chlorides to enable the growth of amorphous layers at low deposition temperatures [1]. An ALD GaAs process could be established, resulting in smooth and stoichiometric films that are amorphous as deposited. Crystallization into the preferred cubic phase was obtained at 350-400˚C, despite the presence of a Ga-rich surface oxide due to air exposure. Irrespective of the excellent step coverage in high aspect ratio structures, we found that these films are prone to delamination. We encountered a comparable challenge with ALD GeSe and $Ge_2Sb_2Te_5$ (GST) using this chemistry, and could demonstrate the benefit of proper surface treatments prior to film deposition to engineer the interface structure and improve layer adhesion. For GeSe, the extension of the existing ALD process [2] to ternary and even quaternary compounds is needed to boost the memory cell performance. We will therefore report on the development of an ALD process targeting GeAsSe deposition. Finally, we explored area-selective deposition (ASD) of chalcogenide materials, as this could greatly simplify the fabrication of complex 3D SCM devices. Our results indicate an impressive selectivity of 96% for GST films of ~22nm on TiN compared to SiO_2, by using the dechlorosilylation chemistry in combination with a dimethylamino-trimethylsilane (DMA-TMS) surface treatment.

[1] Pore et al, ***J. Am. Chem. Soc.***, 2009, **131**, 3478-3480

[2] Haider et al, ***Mater. Adv.***, 2021,**2**, 1635-1643

9:00am **TF2+AP+SE+SS-WeM-4 Plasma-enhanced Spatial ALD of SiO_2 investigated by gas-phase Infrared and Optical Emission Spectroscopy***, M. Mione, V. Vandalon,* Eindhoven University of Technology, Netherlands*; A. Mameli,* TNO-Holst Centre & Eindhoven University of Technology, The Netherlands*; F. Roozeboom,* TNO-Holst Centre & Eindhoven University of Technology, Netherlands*; **Erwin Kessels**,* Eindhoven University of Technology, Netherlands

A spatial atomic layer deposition (ALD) process for SiO_2 using bisdiethylaminosilane (BDEAS, $SiH_2[N(C_2H_5)_2]_2$) and an atmospheric O_2 plasma is reported as well as an investigation of its underlying reaction mechanisms [1]. Within the substrate temperature range of 100-250 °C, the process demonstrates self-limiting growth with a growth-per-cycle between 0.12 and 0.14 nm and SiO_2 films exhibiting material properties *on par* with those reported for low-pressure plasma-enhanced ALD (PEALD) [2].

Gas-phase infrared spectroscopy on the reactant exhaust gases and optical emission spectroscopy on the plasma region are used to identify the species that are generated in the ALD process. Based on the identified species and a calibration procedure, we propose a reaction mechanism where BDEAS molecules adsorb on –OH surface sites through the exchange of one of the amine-ligands upon desorption of diethylamine (DEA, $HN(C_2H_5)_2$). The remaining amine ligand is removed through combustion reactions activated by the O_2 plasma species leading to the release of H_2O, CO_2, CO in addition to products such as N_2O, NO_2, and CH-containing species. These volatile species can undergo further gas-phase reactions in the plasma as indicated by the observation of OH*, CN* and NH* excited fragments in emission. Furthermore, the infrared analysis of the precursor exhaust gas indicated the release of CO_2 during precursor adsorption. Moreover, this analysis has allowed the quantification of the precursor depletion yielding values between 10 % and 50 % depending on the processing parameters. On the basis of these results, the overall surface chemistry of the spatial ALD process of SiO_2 will be discussed.

[1] M. Mione, V. Vandalon, A. Mameli, W.M.M. Kessels, and F. Roozeboom, J. Phys. Chem. C 125, 24945 (2021)

[2] G. Dingemans, C.A.A. van Helvoirt, D. Pierreux, W. Keuning, W.M.M. Kessels, J. Electrochem. Soc. 159, H277 (2012)

9:20am **TF2+AP+SE+SS-WeM-5 Role of Al in Enhancing Growth Rate and Crystallinity in Chemical Vapor Deposition of $Hf_{1-x}Al_xB_2$ Coatings Below 300 °C***, **Kinsey Canova**[1], S. Shrivastav, C. Caroff, L. Souqui, G. Girolami, J. Krogstad, J. Abelson,* University of Illinois at Urbana-Champaign

Transition metal diborides are desirable as hard, low-friction, and wear-resistant coatings for applications in extreme environments. To survive high temperatures, the coatings must have a very low rate of microstructural evolution and must resist oxidation, in particular the loss of boron via evaporation of boron oxide. We previously showed that amorphous HfB_2 films can be deposited by chemical vapor deposition (CVD) using a borohydride precursor, $Hf(BH_4)_4$. However, at T > 600 °C, those coatings crystallize and densify, which leads to cracking, and they oxidize readily. Here, we co-flow an aluminum precursor, trimethylamine alane (TMAA), to deposit ternary $Hf_{1-x}Al_xB_2$ alloy films by CVD at temperatures ≤ 300 °C. This affords excellent film deposition and properties: (i) Al incorporation substantially increases the reaction rate of the HfB_2 precursor, yet the growth still gives good conformal coverage over all surfaces in deep features. (ii) The as-deposited films are nanocrystalline, and the lattice parameters are consistent with a random alloy on the metal sublattice, as opposed to a mixture of HfB_2 and AlB_2 grains. (iii) No elemental Al is detected, so there is not a mechanically soft, low-melting phase. (iv) Annealing films to 700 °C in air creates an Al_2O_3 surface layer that protects the underlying film, and negligible grain growth is observed. To determine a cause of the enhanced growth rate, we performed a matrix of growth experiments vs. precursor pressures and temperature; the Al

[1] **TFD James Harper Award Finalist**

incorporation rate, which is proportional to TMAA flux, has the strongest effect on rates. We hypothesize that Al consumes the excess boron from the HfB_2 precursor – which contains four boron atoms for every Hf atom – and forms AlB_2. This overcomes the probable rate limiting step of HfB_2 deposition, i.e., the associative desorption of excess boron from the growth surface as B_2H_6, and it is consistent with the improved film crystallinity. Finally, this study provides a guide to the parameters controlling growth rate and composition.

9:40am **TF2+AP+SE+SS-WeM-6 Pushing the Limits of ALD Infilling to Produce Macroscopic Nanocomposites***, **Benjamin Greenberg**, K. Anderson, A. Jacobs, J. Wollmershauser, B. Feigelson,* U.S. Naval Research Laboratory

Atomic layer deposition (ALD) infilling is a reliable and popular technique for producing nanocomposite thin films. Typically, ALD precursor dose times on the order of 1 s are sufficient for infiltrating and conformally coating the pores of nanoparticle (NP) networks with thickness on the order of 1 µm or less. In principle, the application space for this nanocomposite production method could be expanded significantly by increasing the NP network thickness to 1 mm or greater. In this work, we investigate the possibility of achieving this scale-up through increasing the ALD precursor dose time by three orders of magnitude. We hydraulically press aluminum oxide nanopowder with particle size on the order of 100 nm to form nanoporous compacts with ~2 mm thickness and ~50% solid volume fraction, and we coat the pores with either Al_2O_3 or ZnO by static-dose ALD, holding precursor vapor in the ALD chamber for >1,000 s per half-cycle. For both coatings, we analyze the ALD chamber pressure traces to understand precursor diffusion and reaction kinetics, and we compare our results to predictions based on a Knudsen diffusion model. For the ZnO coating, we use electrical conductivity measurements, X-ray crystallography, scanning electron microscopy, and energy-dispersive X-ray spectroscopy to evaluate coating composition and uniformity within the nanocomposite, and we compare the ZnO-infilled-Al_2O_3 nanocomposite to a compact of core/shell Al_2O_3/ZnO NPs produced by particle ALD (pALD) in a rotary reactor. Preliminary data suggest that uniform infilling of a macroscopic NP network is possible provided that it can be carried out at a temperature sufficiently low to prevent precursor decomposition.

Thin Films Division
Room 316 - Session TF3+MS-WeM
Simulations and Machine Learning Applications for Thin Films

Moderator: Angel Yanguas-Gil, Argonne National Lab

11:00am **TF3+MS-WeM-10 What an Experimentalist Needs from Computational Materials Science (Including Machine Learning) – Studies in Semiconductor Processing and Metrology***, **Rafael Jaramillo**,* MIT **INVITED**

I will present a view on computational materials science and machine learning, from the perspective of an experimentalist working primarily on compound semiconductors. I will first present uses of computation within my own group. These include computational thermodynamics to guide materials design and synthesis, atomistic modeling of deep levels in semiconductors, finite-element modeling of mechanical and acoustic phenomena, and machine learning models of optical metrology to improve materials discovery and microelectronics manufacturing. In many cases, our computations are limited by challenges that are beyond our expertise as experimentalists. With these challenges in mind, I will then highlight several outstanding needs from the computational science community, illustrated by ongoing research projects:

(1) We pioneered the synthesis of chalcogenide perovskite thin films by gas-source molecular beam epitaxy (MBE). Our successes pose questions of process optimization, particularly related to connections between precursor selection, processing temperature, and crystal quality. There is a need for multi-scale modeling of crystallization at solid-vapor interfaces, including highly-non-thermodynamic conditions such as plasma processing, to de-risk the development of manufacturing-compatible deposition methods.

(2) We discovered that chalcogenide perovskites have the strongest low-frequency dielectric response among VIS-NIR semiconductors. The only other family of semiconductors with comparable dielectric response are halide perovskites. We also discovered that chalcogenide perovskites have, in common with their halide cousins, slow non-radiative excited-state recombination. These observations pose the question of how, exactly, soft phonon spectra affect Schottky-Read-Hall (SRH) recombination rates. Polarons may be relevant. Exact calculations of SRH capture cross sections for particular materials, coupled to a Fröhlich model of electron-phonon interactions, would shed light on these open questions in solar cell materials physics.

(3) Native oxidation of chalcogenide layered and two-dimensional semiconductors (notably including transition metal dichalcogenides, TMDs) needs to be well understood for microelectronics fabrication, and presents unique opportunities for ultra-scaled logic and memory devices. We have used theory and experiment to describe TMD native oxidation processes. However, reactive molecular dynamics simulations combined with advanced data analytics are needed to accelerate progress towards device technology that would be advanced and manufacturable.

11:40am **TF3+MS-WeM-12 Computational Analysis and Design of Precursors for ALD and CVD of Metals***, S. Elliott, A. Chandrasekaran, S. Tiwari, A. Fonari, D. Giesen,* Schrödinger*; **Casey Brock**,* Schrödinger

Understanding a deposition process depends to a large extent on understanding the chemical and physical properties of the precursor molecules. Volatility, reactivity and thermal stability are the three key precursor characteristics needed for chemical vapor deposition (CVD) and atomic layer deposition (ALD), although properties such as melting point, viscosity, synthetic cost and nucleation behavior are also important. Quantifying these characteristics for known precursors can help trouble-shoot an existing process, and designing novel precursors with optimum characteristics is a robust way to improve a process. We illustrate these points on the example of beta-diketonate-based Pd(II) precursors for the deposition of palladium metal. The aim is to find the optimum ligand combination in both homoleptic and heteroleptic complexes.

Precursor volatility often dictates the lower limits of temperature and pressure at which a process can be run. We use a machine-learning model of volatility to see the effect of ligand identity on this property. Specifically, cyclopentadienyl and allyl ligands are found to lower the evaporation temperature to <100 degrees C in the 1-5 Torr pressure range. The other end of the process window is determined by thermal decomposition. For Pd(hfac)2 and formalin experiments show a narrow ALD window between 200 and 230°C, followed by decomposition at higher temperatures. We therefore use density functional theory (DFT) to assess the thermal stability of candidate complexes. We exclude those heteroleptic complexes that DFT predicts to be impossible to synthesize because of ligand exchange. We find that the poor stability of thd complexes can be overcome by switching to fluorinated ligands. We also present quick and approximate measures of the reactivity towards reduction to metallic Pd, whether by CVD or ALD, and compare these with more time-consuming DFT calculations of the surface chemistry.

The computational tools for these properties have been automated to the level where they can be integrated into a team's R&D workflow for routinely assessing current precursors or discussing new ones, so that lists of molecules can be generated and ranked according to the key characteristics for a particular process and application area.

12:00pm **TF3+MS-WeM-13 Dopant-selective Atomic Layer Deposition of Metals for Bottom-up Nanoelectronics***, **Nishant Deshmukh**,* Georgia Institute of Technology, USA*; D. Aziz, A. Brummer, M. Filler,* Georgia Institute of Technology

The entirely bottom-up fabrication of nanoelectronic devices promises electronics with an unprecedented combination of performance and scalability. A long-standing challenge has been the bottom-up fabrication of nanoscale features on nanoscale semiconductors. Bottom-up methods can create suitable semiconductor structures, but top-down methods are needed for other important device features, such as contacts or gate stacks. For example, Si nanowire pn diodes can be readily fabricated with the vapor-liquid-solid (VLS) growth method; however, lithography is still necessary to define contacts to the p and n segments. Here, we report a dopant-selective atomic layer deposition (ALD) process to deposit metal thin films suitable for constructing fully bottom-up pn diodes. Briefly, undecylenic acid, a bifunctional self-assembled monolayer (SAM), is blanket attached to the Si surface. Exposure to KOH removes it from the surface of heavily-doped (~10^{20} cm^{-3}) p-type and n-type Si while it remains on lightly-doped (~10^{14} cm^{-3}) Si. Subsequent Pt ALD yields deposition only on the heavily-doped Si. X-ray photoelectron spectroscopy (XPS) shows that the ratio of Pt deposition on the heavily-doped to lightly-doped Si can

be as high as 130. We suspect that this high selectivity results from undecylenic acid attaching to lightly-doped Si through its alkene group, and to heavily-doped Si through its carboxylic acid group. This difference in attachment results in KOH being able to remove undecylenic acid only from the heavily-doped Si, thus allowing Pt to deposit.

Advanced Surface Engineering Division
Room 317 - Session SE+MN+PS+TF-WeA

Vapor Deposition Technologies and New Trends in Surface Engineering

Moderators: Jianliang Lin, Southwest Research Institute, **Filippo Mangolini**, The University of Texas at Austin

2:20pm **SE+MN+PS+TF-WeA-1 Breaking the Back-Attraction by Bipolar HiPIMS Bursts*, Rajesh Ganesan,*** University of Illinois at Urbana-Champaign **INVITED**

Limiting the back-attraction of ions is crucial to increase the deposition rate in HiPIMS processing. Back-attraction can be considerably limited by bipolar plasma bursts in which a positive voltage pulse is applied instantaneously after the negative voltage pulse. Energy-resolved mass spectroscopy confirms that, in addition to the increased flux, the energy of the target metal ions travelling from the target to the substrate is also increased, as a function of positive pulse length. Amorphous carbon coatings have been deposited by bipolar HiPIMS (BiPIMS) as a case study. The increased energy of the depositing flux led to a higher density of the carbon coatings and a significant reduction in the incorporation of the sputter gas atom, argon, was observed in the coatings. Langmuir probe measurements suggest the optimum plasma density window to minimize arc generation and reduce the probability of generated arcs moving away from the target racetrack, which results in smoother coatings. BiPIMS voltage pulses of optimized length and magnitude help to coat high quality amorphous carbon coatings with excellent machining functionalities.

3:00pm **SE+MN+PS+TF-WeA-3 Experimental and Theoretical Study of the Thermal Shock Behavior of MAX Phase Thin Films*, Matej Fekete,*** *C. Azina, P. Ondračka, L. Löfler, D. Bogdanovski,* RWTH Aachen University, Germany*; D. Primetzhofer,* Uppsala University, Sweden*; M. Hans, J. Schneider,* RWTH Aachen University, Germany

Components subjected to rapid temperature changes are prone to thermal shock, which may result in damage or catastrophic failure. Thus, thermal shock resistance is one of the performance-defining properties for an application where extreme temperature gradients are required. The thermal shock resistance can be described by the thermal shock parameter (R_T), which depends on the flexural strength, thermal conductivity, Poisson's ratio, linear coefficient of thermal expansion, and elastic modulus. In this study, these thermomechanical properties of Ti_3AlC_2 and Cr_2AlC MAX phase coatings are investigated by both experiment and theory. The R_T of Ti_3AlC_2 obtained through quantum mechanical predictions is in good agreement with the experimentally obtained R_T. However, for Cr_2AlC, the theoretical predictions result in approximately two times larger R_T than experiments. This difference may be caused by omitted spin-polarization in the calculation of the electronic part of the thermal conductivity. Correlating the studied MAX phase thin films, both experiments and theory indicate superior facture behavior of Ti_3AlC_2 in comparison to Cr_2AlC. This is attributed primarily to the higher thermal conductivity of Ti_3AlC_2.

4:20pm **SE+MN+PS+TF-WeA-7 Combinatorial Application of Advanced Characterization Methods to Illuminate the Role of Interfaces in Multilayer Coatings*, Nina Schalk,*** *C. Kainz, F. Frank,* Montanuniversität Leoben, Austria*; C. Czettl, M. Pohler,* CERATIZIT Austria GmbH, Austria*; M. Tkadletz,* Montanuniversität Leoben, Austria **INVITED**

The microstructural characterization of multilayer coatings and their interfaces is challenging, especially if the layer thicknesses are only in the nm range. Within this talk, two model coatings are used to evaluate the suitability of several characterization methods for the investigation of their microstructure and interfaces on different length scales. The fine grained cathodic arc evaporated ZrN/TiAlN and the rather coarse grained chemical vapor deposited TiCN/TiC multilayer model coatings exhibit different bilayer thicknesses and layer thickness ratios and thus allow also insight into the effect of the layer thickness on coherency, grain size and strain state. Starting with methods such as scanning electron microscopy and laboratory X-ray diffraction, an overview of the coating structure and information on the average strain/stress state can be obtained. Depending on the grain size and individual layer thickness, high resolution electron backscatter diffraction allows a more detailed insight into the microstructure and strain state of individual layers. In addition, information about gradients of strain/stress across the coating thickness is accessible by cross-sectional X-ray nanodiffraction. However, for a detailed investigation of the interfaces, the application of high resolution methods such as transmission electron microscopy and atom probe tomography is indispensable, providing information about lattice misfits and related strain evolution in the layers as well as on the sharpness of the interfaces in terms of elemental distribution down to the atomic scale. The present talk highlights that for the characterization of the different multilayer systems the combinatorial application of different characterization methods is possible and reasonable.

5:00pm **SE+MN+PS+TF-WeA-9 Influence of Al-Content on Structure, Mechanical Properties and Thermal Stability of Reactively Sputtered AlTaTiVZr High-Entropy Nitride Coatings*, Alexander Kirnbauer*[1]**, TU Wien, Austria*; S. Kolozsvári,* Plansee Composite Materials GmbH, Germany*; P. Mayrhofer,* TU Wien, Austria

In the field of materials research, a novel alloying concept, so-called high-entropy alloys (HEAs), has gained particular attention within the last decade. These alloys contain 5 or more elements in equiatomic or near-equiatomic composition. Properties, like hardness, strength, and toughness can be attributed to the specific elemental distribution and are often superior to those of conventional alloys. In parallel to HEAs also high-entropy ceramics (HECs) moved into in the focus of research. These consist of a solid solution of 5 or more binary nitrides, carbides, oxides, or borides. Within this work, we investigate the structure and, mechanical properties of thin films based on the high-entropy concept, with particular emphasis on the thermal stability, dependent on the Al content in AlTaTiVZr thin films.

Therefore, AlTaTiVZr nitride coatings were reactively sputtered in a lab-scale sputter deposition facility using a single powder-metallurgically produced composite target and Al cubes placed along the racetrack to increase the Al content within the coatings. The coatings in as-deposited state show a fine-columnar growth and crystallise in a single-phase face-centred cubic (fcc) structure. The hardness of our coatings in as-deposited state is ~32.8 GPa and relatively independent on the Al-content. We studied the influence of the Al content on the thermal stability by investigating the structural evolution of our coatings by DSC and powder X-ray diffraction, as well as nanoindentation upon vacuum annealing. The study reveals a distinct influence of the Al-content on the decomposition of the solid solution into an fcc-matrix and Al-rich domains.

5:20pm **SE+MN+PS+TF-WeA-10 Ternary Transition Metal Diborides – Future Defect Engineered Protective Coating Materials?***, A. Hirle, L. Zauner, C. Fuger, A. Bahr, R. Hahn, T. Wojcik, T. Glechner,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria*; J. Ramm, O. Hunold,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; P. Polcik,* Plansee Composite Materials GmbH, Germany***; Helmut Riedl,*** TU Wien, Austria

In the progression of novel protective thin film materials, the attention for transition metal diborides (TMB_2) substantially increased during the last years. The unique strength of their hybridized covalent bonds combined with their hexagonal close-packed (hcp) structures is a big advantage and limiting factor at the same time. The related brittleness, variety of crystal structures, and stoichiometries depict significant challenges for a broad usage of these structurally imperfect coating materials. Furthermore, the formation of non-adherent and volatile oxide scales is also a major limiting factor.

Within this study, we want to address these specific challenges on various ternary model systems within group IV to VI transition metal diborides (e.g. $TM_{1-y}X_yB_{2\pm z}$ prototypes). As structural defects play a major role for the phase formation of the two characteristic hexagonal structure types (α–AlB_2 vs. ω-W_2B_{5-x}-prototype), the target composition and ionization degree within the plasma, has been systematically correlated with the deposition parameters for non-reactive DCMS and HiPIMS depositions. In addition, different alloying concepts for enhancing the ductile character – by microstructural design of imperfect grain boundary structures [1, 2] – as well as oxidation resistance – up to 1200 °C through Si alloying [3] – of these superhard ternary diborides will be discussed in detail. To describe all these relations comprehensively, we correlated the synthesis parameters with structural and morphological evolution using XRD, HR-TEM, APT, as well as micro-mechanical testing methods. Furthermore, specific aspects have also been described by atomistic modelling (DFT).

Keywords : Ternary Borides; Protective Coatings; Defect Engineering; High Temperature Oxidation;

[1] **2021 ASED Young Investigator Awardee**

[1]T. Glechner, H.G. Oemer, T. Wojcik, M. Weiss, A. Limbeck, J. Ramm, P. Polcik, H. Riedl, Influence of Si on the oxidation behavior of TM-Si-B2±z coatings (TM = Ti, Cr, Hf, Ta, W), Surf. Coat. Technol. 434 (2022) 128178.

[2] C. Fuger, R. Hahn, L. Zauner, T. Wojcik, M. Weiss, A. Limbeck, O. Hunold, P. Polcik, H. Riedl, Anisotropic super-hardness of hexagonal WB2±z thin films, Materials Research Letters. 10 (2022) 70–77.

5:40pm **SE+MN+PS+TF-WeA-11 Influence of Interplay of Substrate Template Effects and Bias Voltage on the Microstructure of Cathodic Arc Evaporated Fcc-$Ti_{0.5}Al_{0.5}N$ Coatings***, Michael Tkadletz, N. Schalk, H. Waldl,* Montanuniversität Leoben, Austria*; B. Sartory, J. Wosik,* Materials Center Leoben Forschung GmbH, Austria*; C. Czettl, M. Pohler,* CERATIZIT Austria GmbH, Austria

Ever since the implementation of hard coatings as wear protection for cutting tools, their microstructural design has been of major interest. While the effect of the deposition parameters, such as the applied bias voltage or the substrate temperature, on the microstructure are frequently investigated and rather well understood, commonly less attention is paid to the used cemented carbide substrates. Yet properties like their phase composition and carbide grain size significantly influence the resulting coating microstructure. Thus, within this work substrate template effects are studied on fcc-$Ti_{0.5}Al_{0.5}N$ coatings grown by cathodic arc evaporation onto cemented carbide substrates with different WC grain sizes. A systematic variation of the bias voltage resulted in coarse, intermediate and fine grained coating microstructures, which revealed substrate template-based coating growth at low bias voltages and bias dominated coating growth at high bias voltages. In addition, a strong influence of the applied bias voltage on the resulting preferred orientation of the deposited coatings was observed, providing the basis to tailor the texture to 100, 110 or 111. Elaborate X-ray diffraction and electron microscopy studies contributed to gain further understanding of the substrate template effects and revealed that implementation of a suitable baselayer offers the possibility to effectively prevent any influence of the used substrate on the microstructural evolution of the coating. Supplementary micromechanical experiments illuminated the impact of microstructure, template and non-template based coating growth on the obtained mechanical properties. The obtained results set the fundament to implement tailored microstructures with designed gradients of crystallite size, preferred orientation and consequently mechanical properties, which, as required, either utilize substrate template effects or avoid them.

6:00pm **SE+MN+PS+TF-WeA-12 Super Hard High Temperature TaC-Based Superlattice Protective Coatings Prepared by Magnetron Sputtering***, **Barbara Schmid**,* TU Wien, Austria*; S. Kolozsvari,* Plansee Composite Materials GmbH, Germany*; P. Mayrhofer,* TU Wien, Austria

Transition metal carbides belong to ultra-high temperature ceramics (UHTC) and are particularly valued for their high thermal and mechanical stability as well as melting points of even above 4000 °C. Therefore, those materials are especially interesting for the application as protective coatings. However, a considerable limitation of these materials is their high inherent brittleness. Inspired by the success of nanolayered superlattice architecture—shown to enhance both hardness and toughness of transition metal nitrides like TiN/CrN or TiN/WN—we developed superlattice films based on TaC. These combinations are motivated by ab initio density functional theory calculations exhibiting large and small shear modulus and lattice parameter misfits. Our coatings are prepared via non-reactive DC and pulsed DC magnetron sputtering using binary carbide compound targets. In our study, we want to compare TaC-based superlattice systems and investigate the influence of the superlattice architecture on material characteristics like mechanical, thermal and electrical properties. Apart from nanoindentation and micromechanical cantilever testing for hardness and fracture toughness, material stability at elevated temperatures as well as thermoelectrical properties are being characterized.

Thin Films Division
Room 316 - Session TF1+AP-WeA

Manufacturing and Scale-Up of CVD and (Spatial) ALD

Moderators: Joe Becker, Kurt J. Lesker Company, **Marceline Bonvalot**, Grenoble Alpes University, France

2:20pm **TF1+AP-WeA-1 Optimizing Vapor Delivery of a Nickel Diazadienyl Complex for Nickel Metal Atomic Layer Deposition***, J. Maslar, **Berc Kalanyan**,* NIST-Gaithersburg*; V. Dwivedi,* NASA*; D. Moser,* EMD Electronics

Nickel metal films find applications in numerous areas, including microelectronics and heterogeneous catalysis.In the case of microelectronics in particular, a nickel metal thermal deposition process that can produce high-purity, thin, conformal films at low deposition temperature is highly desirable.Atomic layer deposition (ALD) is widely used to deposit thin, conformal films when suitable precursors are available.However, because nickel is an electropositive metal, many of the combinations of reducing agent and metal precursor classes employed in more traditional metal thermal ALD processes are not suitable for Ni ALD.In contrast, transition-metal diazadienyl complexes represent a class of precursors that has been used successfully for metal thermal ALD, with the deposition of nickel films achieved using bis(1,4-di-*tert*-butyl-1,3-diazadienyl)nickel [$Ni(DAD)_2$].[1]A complicating factor in the reproducible deposition of nickel metal films with $Ni(DAD)_2$ is that this precursor is a solid at typical delivery temperatures and, in general, delivering a constant flux of a solid precursor can be difficult.Flux variations may not be an issue for an ideal ALD process unless the total precursor dose is insufficient to saturate all surface reactive sites, however, it is not clear what delivery conditions are necessary to provide consistently saturating $Ni(DAD)_2$ doses.The goal of this investigation is to optimize $Ni(DAD)_2$ delivery for nickel ALD and to identify any factors that may lead to irreproducible delivery.To achieve this goal, the dependence of the flux of both $Ni(DAD)_2$ and the DAD ligand (the primary decomposition product under the conditions of this study) on delivery conditions was characterized.The flux of each species was measured simultaneously using a two-channel gas analyzer which employed a broadband ultraviolet-visible source, a beam splitter, bandpass filters for wavelength isolation, and avalanche photodiode detectors.While the results of this investigation specifically apply to $Ni(DAD)_2$ delivery, it is expected that these results should also provide insight into optimizing delivery of other transition-metal diazadienyl complexes, as well as solid precursors in general.

[1] Kerrigan, M. M.; Klesko, J. P.; Blakeney, K. J.; Winter, C. H. Low Temperature, Selective Atomic Layer Deposition of Nickel Metal Thin Films. *ACS Appl. Mater. Interfaces* 2018, 10, 14200−14208.

2:40pm **TF1+AP-WeA-2 Mechatronic Spatial Atomic Layer Deposition: Model-Informed Design for Scalable Manufacturing***, **Daniel Penley**, T. Cho, O. Trejo, K. Barton, N. Dasgupta,* University of Michigan, Ann Arbor

Spatial atomic layer deposition (SALD) holds promise to address the large-scale manufacturing needs of interfacial engineering at the nanoscale. However, the many SALD systems are limited in their ability to tune and dynamically control the full range of key process parameters, such as the depositor head and substrate gap size and parallel alignment. This lack of mechatronic control limits the ability to examine the coupled chemical, thermal, and transport phenomena as a function of SALD process parameters. Additionally, there have been several previous efforts to computationally model the SALD processes. However, there is a general lack of experimentally-validated models to verify the effects of systematically tuning the multitude of process parameters during SALD growth.

Herein we describe a customized SALD system that enables mechatronic control of key process parameters. A showerhead depositor design effectively delivers precursor to the substrate surface while stepper motors and capacitive probes maintain gap size and parallel alignment through multiple axis tilt and closed-loop feedback. Precision motorized stages control the substrate velocity and positioning, *in situ* monitoring actively controls the gas flow rates, and a thermal management system controls process temperature. We developed a three-dimensional COMSOL Multiphysics model to understand the pressure, velocity, and concentration fields of the precursor gas flow within the system geometry. The capability to tune process parameters both physically and digitally allows for the unique ability to experimentally validate and parameterize the computational model to gain further insight into the otherwise difficult to access process area of close-proximity SALD. Using this linked

experimental and modeling approach, we demonstrate the model's ability to predict resulting films from the mechatronic SALD system. With the experimentally-validated model and system, we present a study of the impact of SALD process parameters on the uniformity and quality of deposited SALD films. We then broaden our findings to discuss design implications SALD system design on the manufacturing tradeoffs of quality-throughput-cost-sustainability.

3:00pm **TF1+AP-WeA-3 Atmospheric Pressure Spatial ALD of Al-Doped ZnO: Co-injection vs. Supercycles***, **Mike van de Poll**, B. Macco, E. Kessels,* Eindhoven University of Technology, Netherlands

Atmospheric pressure spatial atomic layer deposition (ALD) is particularly interesting for high volume, low cost applications, because of its exceptionally short deposition times compared to temporal ALD.

For doped and compound materials, such as transparent conductive oxides, the electrical and optical properties are typically closely related to their composition. This makes accurate compositional control essential for high quality films. Spatial ALD of doped and compound materials generally follows one of two approaches. Supercycles can be formed by alternating two ALD cycles with different precursors, where the ratio between both cycles determines the composition of the deposited film. Alternatively, in the so called co-injection approach, the precursors can be dosed simultaneously. Here, the composition is determined by the precursor flows ratio.

In this work, ZnO:Al thin films were deposited using spatial ALD, with diethylzinc (DEZ) and dimethylaluminum isopropoxide (DMAI) as zinc and aluminum precursors, respectively, and H_2O as co-reactant. The supercycle and co-injection approaches were used, and the cycle ratio and mixing ratio were varied to alter doping concentrations. The films were capped with a layer of Al_2O_3 to shield from the ambient, and to mitigate hydrogen effusion. Electrical and optical properties of the samples as-deposited, and after stepwise anneal, were extensively studied.

Co-injection and supercycles resulted in the successful deposition of ZnO:Al films with optical and electrical properties (e.g., resistivity = 1.73 mΩcm, mobility = 9.6 cm^2/Vs, carrier concentration = $3.75\cdot10^{20}$ cm^{-3}) similar to temporal ALD ZnO:Al. Furthermore, the extensive study of these approaches led to identification of their advantages and disadvantages. Co-injection results in films with low resistivity as-deposited, due to homogeneous distribution of dopants. However, obtaining low Al doping levels can be practically challenging because low DMAI flow is required. Meanwhile, supercycles give precise compositional control by changing the cycle ratio, but result in dopant planes with low doping efficiency, and post-deposition anneal is required. After annealing the results are similar to co-injection.

Currently, our work focusses on the innovative approach of co-injection supercycles. Here, pure DEZ and co-injection DEZ/DMAI cycles are alternated, allowing additional compositional control by tuning both the DMAI flow during the doping cycle, and the cycle ratio. With co-injection supercycles we aim to combine the advantages of both dosing approaches. Initial films have been deposited and the full study will be presented at the conference.

3:20pm **TF1+AP-WeA-4 Manufacturing of ALD-enhanced Li-ion Batteries via Particle ALD Coatings And R2R ALD on Separators***, **Markus Groner**, A. Dameron, B. Hughes, D. Lewis, J. Keene, M. Martinez, J. Burger, M. Rodgers, J. Ragonesi,* Forge Nano*; J. Li,* Oak Ridge National Laboratory, China*; W. Steenman, K. Livingston,* Oak Ridge National Laboratory

ALD processing equipment for coating anode, cathode, and separator materials at scale has been developed to demonstrate ALD-enhanced Li-ion battery manufacturing. The promising performance enhancements seem previously in coin cells for ALD coated anode and cathode powders are now being validated in pouch cells. Thin ALD coatings can stabilize graphite and NCM materials, yielding improved capacity retention and rate performance, especially at higher voltages. Particle ALD coating tools are available for coating powders at the tons-per-day scale, both in semi-batch and continuous ALD versions. Additionally, ALD coatings on separators enhance electrolyte wetting and thermal stability, which should lead to improvements in the time & energy intensive filling/formation/aging steps as well as safety. A true roll-to-roll ALD tool for coating separators with alumina ALD films has been designed and built. Over the next year, this R2R tool will be integrated with a slitter and a pouch cell stacker. The performance improvements of the ALD-coated anode and cathodes, combined with the benefits of R2R ALD-coated separator, promise reductions in the cost/time/energy of battery manufacturing via ALD-enhanced Li-ion batteries.

Thin Films Division
Room 316 - Session TF2-WeA

Solution Based and Graphene or Polymer Deposition Techniques

Moderators: Parag Banerjee, University of Central Florida, **Mark Losego**, Georgia Institute of Technology

4:20pm **TF2-WeA-7 The Truth About Graphene - Where Is It and Why It Is Taking This Long to Get Here***, M. Baraket, **Michael Stanford**,* General Graphene Corporation

Graphene is a monolayer of sp^2-bonded carbon atoms assembled in a honeycomb lattice structure that has attracted incredible attention for its many promising properties. It has been said that Graphene can do anything you need - except get out of the laboratory. The CVD-grown large area graphene has yet to become useful outside the laboratory due to its cost which is usually well over $10,000 dollars per square meter. Consequently, graphene's accessibility has been severely restrained with virtually no chance to integrate into industrial applications requiring high product volumes. To address this, General Graphene has scaled-up the graphene growth using an atmospheric pressure CVD process to produce cost effectively truly large-scale mono and multilayers graphene. This led us to produce different graphene types from polycrystalline graphene grown on polycrystalline copper to single oriented grown on single oriented copper to various forms of multilayer. All this can be produced with a single machine with production rates exceeding >30,000 m^2/year. Now that costs and production are in line with industrial applications – the final step is to integrate graphene into targeted applications where its unique properties and abilities provide significant competitive advantages. On the other hand, there is not a single transfer method that works for all applications. This leads to a variety of transfer methods, each with their strengths and weaknesses.

In this talk a brief history of graphene will be presented with emphasis on the challenges faced in growth and transfer along with current state-of-the-art applications with real-world performance and cost data.

4:40pm **TF2-WeA-8 Initiated Chemical Vapor Deposition (iCVD) for Shape-Programmed Polymer Nanoparticles***, **Rong Yang**,* Cornell University

Shape-programmed polymer nanoparticles (PNPs) represent a critical opportunity to advance research in small molecule drug delivery, self-assembly for soft robotics, and metamaterials with emergent properties. Extant techniques like emulsion polymerization commonly used to synthesize PNPs primarily produce particles that are spherically shaped. To achieve non-spherical PNPs, time-consuming solution-based protocols are commonly required, along with additional fabrication and purification steps. The limited selection of monomers, restricted by their solubility, leads to a narrow range of PNP shapes and chemistries, whose deployment is further hindered by the laborious and costly synthesis. Here we present the rapid synthesis of shape-programmed PNPs without the need for nano/microfabrication, enabled by two fresh strategies revolving around initiated chemical vapor deposition (iCVD) polymerization.

The first strategy is a novel template- and solvent-free technique we recently developed, namely condensed droplet polymerization (CDP), which delivers unprecedented flexibility in PNP synthesis. With CDP, particle sizes and dimensions could be varied continuously, from sub-10 nm to above 1 µm. As a proof-of-principle, we demonstrated the synthesis of polymer nanodomes (hydrophilic, hydrophobic, cross-linked, fluorinated, biocompatible) within minutes (seconds for polymerization).

The second strategy is to leverage structured liquids, such as liquid crystals, as templates for the polymerization with reactants, i.e., monomers and initiators, delivered with picomole precision in the vapor phase. The precise delivery of reactants allows polymerization to proceed without disturbing the dynamic structures of liquid templates. A variety of shapes, including nanospheres, domes, disks, and porous networks could thus be obtained using a single technique.

These novel strategies build upon an existing manufacturing instrument, i.e., iCVD, and hence can be scaled down for decentralized manufacturing, or scaled up for industrial production in semi-continuous roll-to-roll fashion. The ability to manufacture shape-programmed soft materials is critical for advancing a wide cross-section of applications ranging from soft robotics to tough yet injectable implants.

5:00pm **TF2-WeA-9 Synthesis, Properties and Applications of Donor-Acceptor Conductive Polymers by Oxidative Chemical Vapor Deposition***, **Marek Charyton**, N. Boscher,* Luxembourg Institute of Science and Technology (LIST), Luxembourg

Conjugated polymers (CPs) have recently gained great scientific attention as promising materials for next generation of photo(electro)catalysts due to their unique physical (thermal and chemical stability, light resistance), optical (broad and intensive absorption) and electronic properties (redox potential, excellent conductivity). Many strategies to tailor the photocatalytic performance of CPs was studied, focusing on tuning band gap or enlarge the separation of electron-hole pairs. Alternatively, the photocatalytic properties of CPs can be also modified by their molecular design. Alternating electron-rich (donor, D) and electron-poor (acceptor, A) units along the polymer's backbone highly impact conductivity and reactivity of the designed polymers. However, to enable large-scale fabrication of optoelectronic, organic materials conductive polymers such as CPs have to be synthetised in straight-froward and low-cost processes. Herein, we propose Oxidative Chemical Vapor Deposition (oCVD) as a method that fulfils these requirements. This solvent-free technique allows to form polymers *via* vapor phase deposition directly on the desired surface thus, reducing significantly use of chemical reagents during the process. Moreover, in contrast to conventional liquid methods such aspalladium catalyzed polymerization solubilizing groups are not needed therefore, the method is not limited to only sufficiently soluble monomers. Despites the many merits of oCVD the method have not been widely studied yet. Up to date, the monomers studied in the polymerization *via* oCVD were limited to single electron rich systems like thiophene, EDOT, pyrrole, porphyrins etc.. This presentation describes the development of conductive donor-acceptor conjugated polymer obtained using oCVD method. The conductivity of the obtained thin films was tuned up to 9.75 S cm^{-1} by modification of reaction conditions. Further optical, electrochemical properties and photo(electro)catalytical performance of obtained materials were studied showing the fabricated layers can be used as efficient catalysts for water splitting reaction.

5:20pm **TF2-WeA-10 Effect of doping and annealing on the Optical and Magnetic properties of Sol-Gel deposited NiZn Ferrite films***, **Roni Paul**, S. Kothapally, J. Abu Qahouq , S. Kotru,* The University of Alabama

Ferrite films are of interest in high-frequency applications because of their high resistivity, lower eddy current losses, and better magnetic properties compared to metal alloy films. In this work we investigated the effect of doping (Cu and Co) and annealing on the optical and magnetic properties of NiZn Ferrite films. Films with three different compostions $Ni_{0.5}Zn_{0.5}Fe_2O_4$,$Ni_{0.35}Cu_{0.2}Zn_{0.45}Fe_2O_4$and $Ni_{0.35}Co_{0.2}Zn_{0.45}Fe_2O_4$ were deposited on quartz substrate using the sol-gel technique. The grown films were annealed at 500 and 800°C in a Rapid Thermal Annealing (RTA) furnace. The structural, optical, and magnetic properties of undoped and doped films were studied as a function of annealing temperature using X-ray Diffractometer (XRD), UV-VIS spectrophotometer, and Vibrating Sample Magnetometer (VSM), respectively. Bandgap of the materials was calculated using absorbance data collected from the UV-VIS spectrophotometer. Permeability values were extracted from the hysteresis loop. The $Ni_{0.35}Cu_{0.2}Zn_{0.45}Fe_2O_4$film annealed at 800°C exhibited maximum permeability (33.94) with minimum bandgap (2.5eV). The results will be presented.

5:40pm **TF2-WeA-11 A Scalable Method for Rare Earth Oxide Thin Films by Chemical Solution Deposition***, **Daniel Rodriguez**, A. Edgar, D. Vodnik, I. Usov,* Los Alamos National Laboratory

Rare-earth metals are a diverse group of elements with properties found nowhere else on the periodic table, and when in their oxidized forms, they exhibit unique traits, such as corrosion resistance to molten metals. In this study, we have applied a chemical solution deposition (CSD) process for coating stainless steel (SS) with thin films of both erbia (Er_2O_3) and yttria (Y_2O_3).

The focus of this talk will discuss different approaches for depositing rare-earth oxides onto SS304/SS316 geometries by both dipping and spraying. For dipping techniques, the formation of Er_2O_3 and Y_2O_3 coatings takes advantage of metal-nitrate solution chemistry, and its transformation into metal-oxide by both thermal annealing and ultra-violet photo-curing. For spray coating (Fig.1), deposition of Y_2O_3 involves deployment of aerosols with inclusion of binding agents such that the oxide is physically stable on the substrate, but also by incorporating substrate treatments to improve its chemical bonding. The results will reflect how fine adjustments to CSD methods leads to improved adhesion strength, composition, uniformity, and reproducibility of both coating thickness and micro-structure. Last, the scalability of CSD will be explained and compared to chemical and physical vapor deposition methods.

The outcome of this work is expected to reduce cost of the metal casting process and provide direct economic and environmental impact. In addition, there are interesting fundamental questions about the properties of rare-earth materials. Therefore, by identifying materials with practical applications, more experiments can be done to further understand the underlying physics and chemistry.

Electronic Materials and Photonics Division
Room 304 - Session EM+MN+TF-ThM

Wide and Ultra Wide Band Gap Materials and Devices

Moderators: Erica Douglas, Sandia National Laboratories, **Rehan Kapadia**, University of Southern California, **Rachael Myers-Ward**, U.S. Naval Research Laboratory

8:00am **EM+MN+TF-ThM-1 What Can We Do With Ga_2O_3?**, ***Man Hoi Wong,*** University of Massachusetts Lowell **INVITED**

The past few decades have witnessed technological innovations driven by physical electronics solutions embodying novel materials and device concepts that fundamentally change our lives today. Ultrawide-bandgap semiconductors represent a new area of intensive research covering a wide spectrum of materials, physics, devices, and applications. As the critical electric field of avalanche breakdown increases super-linearly with increasing bandgap energy, ultrawide-bandgap semiconductors can address critical needs across many areas including energy-efficient power switching, radio-frequency power, and electronics in harsh thermal or radiation environments. I will illustrate efforts to pursue these visions with Gallium Oxide (Ga_2O_3) devices, which have been making rapid strides thanks to ongoing breakthroughs in crystal growth and device processing technologies. Demonstrations of multi-kilovolt breakdown, normally-off operation, vertical device concepts, and heterostructures have positioned Ga_2O_3 devices as relevant contenders for practical applications. In this talk, the achievements on various types of Ga_2O_3 power switches and rectifiers will be reviewed. Materials science pertinent to the implementation of those device concepts will be highlighted. Several approaches to address challenges related to field management and doping will be discussed, using our recent work on enhancement-mode Ga_2O_3 power transistors as an illustration. We are also developing a novel Ga_2O_3 ultrahigh-speed transistor concept that harnesses quasi-ballistic transport effects through heterojunction engineering to reduce carrier transit delay. Such a device can simultaneously serve as an effective spectroscopy tool for studying hot-carrier dynamics in Ga_2O_3. This as well as other types of Ga_2O_3 quantum devices have seen scant experimental and theoretical developments to date and represent a fertile ground for research.

8:40am **EM+MN+TF-ThM-3 Controlled Growth of Epitaxial Ga_2O_3 Polymorphs for Ultra-Wide Bandgap Semiconductor Devices**, ***Lisa Porter,*** *K. Jiang, J. Tang, M. Cabral, R. Davis,* Carnegie Mellon University, USA

Gallium oxide (Ga_2O_3) is attracting increased interest for electronics that can operate in extreme conditions, such as high power, high temperature and high radiation fluxes. This ultra-wide bandgap semiconductor has an interesting feature in that it exists in different phases, or polymorphs. β-Ga_2O_3 is thermodynamically stable at atmospheric conditions up to its melting point and is therefore the phase produced in melt-grown, single-crystal substrates.Epitaxial films of the other metastable polymorphs, however, are also of interest because they possess unique properties – such as high spontaneous polarization, ferroelectricity, or ferromagnetism – that could lead to new types of heterostructure devices.In this presentation we will summarize our results on the growth of epitaxial films of phase-pure vs. mixed-phase ε(κ), β, and γ-Ga_2O_3 using metal-organic chemical vapor deposition.We will focus on variables (temperature, triethylgallium (TEG) flow rate, and type of substrate) that have led to optimum control over the resulting polymorph and its microstructure, as characterized using x-ray diffraction (XRD), scanning electron microscopy, and high-resolution transmission electron microscopy (TEM).For example, for growth on (0001) sapphire substrates the phase composition of a 700-nm-thick epitaxial layer – from nominally 100% ε(κ) to 100% β-Ga_2O_3 – can be controlled by varying the substrate temperature (470 °C to 570 °C) and TEG flow rate (0.29 sccm to 2.1 sccm).We also show that nominally single-phase γ-Ga_2O_3 and β-Ga_2O_3 epitaxial films are produced under the same growth conditions (in the same growth run) by employing different substrates.High-resolution TEM and XRD ω-2θ and phi-scans suggest that the γ-Ga_2O_3 films are single crystal.

9:00am **EM+MN+TF-ThM-4 Plasma Enhanced-ALD Amorphous Gallium-Oxide Channel Thin Film Transistors for Back-End-of-Line Integration**, ***Charlotte Van Dijck,*** Helmholtz-Zentrum -Berlin für Materialen und Energy, Germany; *F. Maudet,* Helmholtz-Zentrum-Berlin für materialen und Energy, Germany; *S. Banerjee, V. Deshpande, C. Dubourdieu,* Helmholtz-Zentrum Berlin für Materialen und Energy, Germany

Amorphous metal oxide semiconductors exhibit promising properties such as high mobility at low deposition temperatures (< 400°C) and hence are widely investigated as channel materials for thin film transistors (TFT). The low processing temperature also enables their integration on the back-end-of-line (BEOL) of Si CMOS circuits for More-than-Moore applications. While amorphous Indium Gallium Zinc Oxide (IGZO) and Indium Zinc Oxide (IZO) are the most studied amorphous metal oxides for TFT applications, amorphous gallium oxide (a-GaO_x) is interesting due to its ultrawide bandgap (~4.9 eV) combined with the ability to control the carrier density by varying the oxygen content in it [1]. Thus, a-GaO_x has potential for high voltage TFT, sensing, and memristive device applications. There have been few reports of a-GaO_x TFTs with pulsed laser deposition or solution processing, yet a detailed study of TFTs featuring ALD based a-GaO_x channel has not been reported up to now.

Here TFTs with a-GaO_x channel deposited with plasma-enhanced atomic layer deposition (PE-ALD) are discussed. PE-ALD allows for relatively low deposition temperatures (~ 250°C), uniform and conformal films. We recently showed that the current through the a-GaO_x layer can be increased with shorter O_2 plasma exposure times during PE-ALD as it increases the number of sub bandgap defects in the oxide [2]. We present a detailed study of a-GaO_x back-gated TFTs deposited with short (1s) O_2 plasma times to obtain a conductive channel. We discuss the main device characteristics such as subthreshold slope (SS), threshold voltage and ON current and their dependence on the a-GaO_x channel length and thickness (22, 50, 75 nm) with 20 nm ALD Al_2O_3 as gate oxide. Transistors with SS < 150 mV/dec and an ON/OFF ratio of 10^5 have been shown for a channel length of 6 µm. Impact of encapsulation of the GaO_x channel with in situ ALD-grown Al_2O_3 and ex situ PECVD-grown SiO_2 on the hysteresis in the transfer characteristics (drain current as a function of gate voltage) of the devices is investigated. A reduction of the hysteresis is achieved after in situ encapsulation of the devices with 2 nm Al_2O_3. Finally, the effect of post-metal annealing on the device performance is discussed.

[1] J. Kim et al. "Conversion of an ultra-wide bandgap amorphous oxide insulator to a semiconductor", NPG Asia Materials 9, e359 (2017)
[2] H. Kröncke et al., "Effect of O_2 plasma exposure time during atomic layer deposition of amorphous gallium oxide." Journal of Vacuum Science & Technology A 39, 052408 (2021)

9:20am **EM+MN+TF-ThM-5 Interface Trap State Analysis of ALD-deposited Gate Dielectrics on Gallium Nitride using a Modified C-ψ_s Procedure**, ***Brian Rummel,*** *L. Yates, C. Glaser, A. Binder, J. Steinfeldt, T. Smith, P. Sharps,* Sandia National Laboratories; *J. Cooper,* Sonrisa Research; *R. Kaplar,* Sandia National Laboratories

The large breakdown electric field strength and high electron saturation velocity of gallium nitride (GaN) make it an attractive semiconductor for high-power and high-frequency applications. GaN-based power systems greatly exceed the power density capabilities of silicon-based systems and currently rival silicon-carbide-based (SiC) systems. However, GaN has been observed to have large interface trap densities at the gate dielectric/semiconductor interface, which inhibits channel mobility in contemporary MIS devices. In addition, typical gate dielectrics are usually deposited by atomic layer deposition (ALD) rather than being thermally grown due to a lack of a high-quality native oxide for GaN. ALD-deposited dielectrics are often associated with a higher concentration of charged oxide defects that promote significant gate leakage currents and induce large shifts in threshold voltages.

Mitigating these defects in wide band gap devices requires reliable characterization techniques suitable for large-scale device fabrication processes. Typical techniques used to characterize the density of interface states for gate dielectrics, such as the high-low method, require unconventionally large probing frequencies to account for fast trap states associated with wide-bandgap materials. The C-ψ_S technique is a quasi-static capacitance-voltage characterization method known for accurately determining surface potentials in MISCAP structures and has been rigorously demonstrated for SiC-based systems. For GaN systems, trap states located at the insulator/GaN interface or within the ALD-deposited

dielectric may lead to dynamic charge/discharge processes that are less prevalent in SiC MIS structures with thermally grown oxides and thereby alter the C-ψ_S analysis. In this work, we successfully adapt the C-ψ_S analytical procedure to GaN-based MIS structures by imposing sensible mathematical conditions and accurately measure interface state densities and oxide charges for ALD-deposited gate dielectrics on n-GaN substrates. A range of post-deposition annealing temperatures is investigated to probe how processing conditions may alter defect states associated with alumina or silicon dioxide gate dielectrics. This work highlights recent progress in our endeavor to fabricate robust GaN-based high-power devices and establish reliable wide-bandgap device characterization procedures.

This work was supported by the DOE Vehicle Technologies Office Electric Drivetrain Consortium managed by Susan Rogers.

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

9:40am **EM+MN+TF-ThM-6 Characterization of Intervalence Band (IVB) Transitions in Boron-Doped Diamond***,*
Souvik Bhattacharya, University of Illinois at Urbana Champaign*; J. Boyd,* Case Western Reserve University*; A. Hossein, S. Reichardt,* University of Luxembourg*; N. Maccaferri,* Umea University, Sweden*; O. Shenderova,* Adamas Nanotechnologies Inc.*; L. Wirtz,* University of Luxembourg*; M. Sankaran,* University of Illinois at Urbana Champaign*; G. Strangi,* Case Western Reserve University

Heavily-doped semiconductors are a special class of materials distinct from both their metal and semiconductor counterparts that can exhibit greatly enhanced electrical conductivity[1] and tunable localized surface plasmon resonances (LSPR)[2, 3]. For example, boron-doped diamond is a wide band-gap, p-type semiconductor which has elicited interest for quantum computing[4] and superconductivity[5]. Here, we characterized boron-doped diamond (BDD) powders by valence electron-energy loss spectroscopy (VEELS) using a scanning transmission electron microscope to reveal potentially new electronic transitions within the valence band. The diamond samples were synthesized commercially by high-pressure-high-temperature (HPHT) methods and obtained from Adamas Nanotechnologies. Basic materials characterization such as high-resolution transmission electron microscopy (HR-TEM), core-EELS and micro-Raman spectroscopy were conducted to assess the structure and crystallinity. The boron doping level was determined to be ca. 800 pm by modelling the Fano line shape and shifts of the zone center peak at 1332 cm-1. The majority of our study then focused on the low-loss region of EELS (i.e., VEELS) where we observed an intense and relatively broad signal on the shoulder of the zero-loss peak (ZLP) that was completely absent in a similarly synthesized undoped (intrinsic) diamond sample. The feature was found to vary spatially within the body of each particle and inferred to correlate with the distribution of boron atoms along the diamond crystal planes. Ab-initio calculations were carried out in support of the experiments to calculate the loss function from the dielectric function. We find that intervalence band transitions of valence band electrons can lead to the observed VEELS features, and that these transitions can couple to form a "plasmon-like" excitation.

References:

1.J. Zhou, H. Zhu, Q. Song, Z. Ding, J. Mao, Z. Ren and G. Chen, Nature Communications 13 (1), 2482 (2022).

2.J. A. Faucheaux, A. L. D. Stanton and P. K. Jain, The Journal of Physical Chemistry Letters 5 (6), 976-985 (2014).

3.Z. Liu, Y. Zhong, I. Shafei, R. Borman, S. Jeong, J. Chen, Y. Losovyj, X. Gao, N. Li, Y. Du, E. Sarnello, T. Li, D. Su, W. Ma and X. Ye, Nature Communications 10 (1), 1394 (2019).

4.P. de Leon Nathalie, M. Itoh Kohei, D. Kim, K. Mehta Karan, E. Northup Tracy, H. Paik, B. S. Palmer, N. Samarth, S. Sangtawesin and D. W. Steuerman, Science 372 (6539), eabb2823 (2021).

5.T. Yokoya, T. Nakamura, T. Matsushita, T. Muro, Y. Takano, M. Nagao, T. Takenouchi, H. Kawarada and T. Oguchi, Nature 438 (7068), 647-650 (2005).

Magnetic Interfaces and Nanostructures Division
Room 330 - Session MI+2D+TF-ThM

Quantum Materials (2D)
Moderator: Zheng Gai, Oak Ridge National Laboratory

8:00am **MI+2D+TF-ThM-1 Exploration of Two Surfaces Observed in Weyl Semimetal $BaMnSb_2$***,*
Zheng Gai*, Q. Zou,* Oak Ridge Natinal Laboratory*; S. Huang,* University of South Carolina*; W. Ko, M. Fu,* Oak Ridge Natinal Laboratory*; Y. Yang, K. Zhao,* Louisiana State University*; S. Crittenden,* University of South Carolina*; E. Plummer,* Louisiana State University*; R. Jin,* University of South Carolina

Single crystalline $BaMnSb_2$ is considered as a 3D Weyl semimetal with the 2D electronic structure containing Dirac cones from the Sb sheet. The unique surface electronic structure can be probed by techniques such as angle-resolved photoemission spectroscopy (ARPES) and scanning tunneling microscopy/spectroscopy (STM/S). However, these techniques require an in-depth understanding of the surface structure and electronic properties. We report experimental investigation of low-temperature cleaved $BaMnSb_2$ surfaces using STM/S and low energy electron diffraction (LEED). By natural cleavage, we find two terminations: one is Ba1 (above the orthorhombic distorted Sb sheet) and another Sb2 (at the surface of the Sb/Mn/Sb sandwich layer). Both terminations show the 2 × 1 surface reconstructions, with drastically different morphologies and electronic properties, however. The reconstructed structures, defect types and nature of the electronic structures of the two terminations are extensively studied. The quasiparticle interference (QPI) analysis also reveals that the surface-projected electronic band structures strongly depend on the surface termination. The existence of defects can greatly modify the local density of states to create electronic phase separations on the surface in the order of tens of nm scale. Our observation on the atomic structures of the terminations and the corresponding electronic structures provides critical information towards an understanding of topological properties of $BaMnSb_2$.

8:20am **MI+2D+TF-ThM-2 Properties of Mn_3Sn Films Grown on Sapphire Substrates Using Molecular Beam Epitaxy***,*
Sneha Upadhyay, Ohio University*; T. Erickson, D. Ingram,* Ohio University*; K. Sun,* The University of Michigan , Ann Arbor*; A. Smith,* Ohio University

The kagome antiferromagnet Mn_3Sn is a fascinating material because it's one of the rare antiferromagnets that exhibits large anomalous Hall and Nernst effects. This opens a new area of research using functional antiferromagnets[1], but for future device applications, it requires fabricating high-quality thin films. There are reports of the controlled growth of Mn_3Sn on substrates like *m*-plane sapphire,[2] Pt/Al_2O_3 (0001)[3,] and others using sputtering growth, but this often can result in polycrystalline films. In this work, we investigate the growth of Mn_3Sn films on *c-plane* sapphire substrates using molecular beam epitaxy. Effusion cells are used for Mn and Sn sources which are calibrated using a quartz crystal thickness monitor. The growth is monitored *in-situ* using reflection high energy electron diffraction and *ex-situ* measurements are carried out using X-ray diffraction, Rutherford backscattering, and cross-sectional scanning transmission electron microscopy. The samples are grown at 500 ± 9°C and 416 ± 9 °C with an Mn: Sn atomic flux ratio of 3.2: 1 on *c-plane* sapphire substrates for 60 mins. We observe streaky RHEED patterns at both temperatures indicating high-quality crystalline growth with 2 different orientations, (0001) and (11-20), which are also backed up by the XRD spectra. STEM verifies ~3:1 Mn to Sn stoichiometry but also reveals discontiguous films. After optimizing the growth conditions, the next phase of the study is to begin *in-situ* scanning tunneling microscopy and spin-polarized STM studies of the structural, electronic, and magnetic properties of the *as-grown* Mn_3Sn surfaces, and in this presentation, we plan to present initial results.

The authors acknowledge support from the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering under Award No. DE-FG02-06ER46317. The authors would like to thank Dr. Stinaff and his students for back coating the sapphire substrates.

[1] S. S. Zhang et al., "Many-body resonance in a correlated topological Kagome Antiferromagnet", Physical Review Letters 125, 046401 (2020).

[2 S.] Oh, T. Morita, T. Ikeda, M. Tsunoda, M. Oogane, and Y. Ando, "Controlled growth and magnetic property of a-plane-oriented Mn3Sn thin film", AIP Advances 9,035109 (2019).

[3] Y. Cheng, S. Yu, M. Zhu, J. Hwang, and F. Yang, "Tunable topological Hall effects in noncollinear antiferromagnets Mn3Sn/Pt bilayers", APL Materials 9, 051121 (2021).

8:40am **MI+2D+TF-ThM-3 Interfacial Magnetism in Oxide Heterostructures*, Alex Demkov,*** The University of Texas at Austin **INVITED**

New functionalities and unexpected electronic structures can emerge in artificially engineered complex oxide heterointerfaces due to the coupling of multiple physical properties such as ferroelectricity, ferromagnetism, conductivity, charge transfer, etc. Here, we discuss heterointerfaces involving perovskite oxides $SrTiO_3$, $LaAlO_3$, and $BaTiO_3$, as well as a rock salt ferromagnetic semiconductor EuO. Combining theoretical analysis, experimental growth, and characterization techniques with atomic level resolution, we highlight some of these intriguing emergent interfacial phenomena. We consider several means of creating a two-dimension carrier gas, through band offset engineering, polarization doping, and oxygen vacancy doping. In addition, we also discuss ways of manipulating these electron/hole gases and their potential applications in new electronic devices.

Starting from the pioneering discovery of a 2DEG at the LAO/STO interface, interfaces of transition metal oxides have been at the center of many theoretical and experimental studies. This two-dimensional carrier gas is rather different from the one occurring in semiconductor heterostructures. Its origins and mechanisms of spatial localization are rather complex. Thanks to modern experimental and theoretical techniques, one can identify which of these mechanisms are actually present at a given interface. In some cases, we can also tailor the choice of specific materials where one mechanism dominates, allowing us to study that particular mechanism in more detail.

Owing to relatively large band gaps and the presence of occupied as well as empty ***d*** and***f*** states, the oxide interfacial 2DEG shows a higher degree of spatial confinement.It is a unique physical system where, in the span of just about a nanometer, one can create strong interactions between multiple order parameters leading to phenomena that in the bulk are either very small or forbidden by symmetry. Besides the fundamental physics interest, these multi-functional interfaces may one day be utilized for technological applications.

The work has been supported by the Air Force Office of Scientific Research under grants FA9550-18-1-0053 and FA9550-12-10494, the Texas Advanced Computing Center, and by the National Science Foundation under grants IRES–1358111.

9:20am **MI+2D+TF-ThM-5 Epitaxial 2D Van Der Waals Magnets*, Roland Kawakami,*** Ohio State University **INVITED**

In this talk, I will discuss our latest advances on the epitaxial growth of 2D van der Waals (vdW) magnets and their integration with topological insulators (TI). This work is motivated by the realization of topological phases such as the quantum anomalous Hall effect and highly efficient spin-orbit torque produced by TIs. We have focused on integrating 2D magnets $MnSe_2$, Fe_3GeTe_2 (FGT) and $CrGeTe_3$ (CGT) with TIs Bi_2Se_3 and Bi_2Te_3.

Our initial studies of $MnSe_2$ growth on Bi_2Se_3 showed a tendency for the interdiffusion of Mn into the Bi_2Se_3. While this was initially undesirable, this ultimately led to the synthesis of $MnBi_2Se_4$ (MBS), a new magnetic topological insulator. This is a vdW material with septuple layer (Se-Bi-Se-Mn-Se-Bi-Se) base units, similar to its cousin $MnBi_2Te_4$ (MBT). However, the vdW phase is not the thermodynamically stable phase and bulk crystals do not exist, so the epitaxial stabilization of MBS creates the opportunity to explore the magnetic and topological properties of this material. We find that MBS is a layered antiferromagnet, similar to MBT, but a difference is that the magnetic moments lie in the plane of the film. Angle resolved photoemission experiments show the presence of a topological surface state with Dirac dispersion.

For bilayers of 2D magnets and TIs, we have focused on FGT and CGT films. A key step has been the optimization of FGT by studying its growth on Ge(111) substrates. Here, we learned that kinetics play an important role in the epitaxial growth. By varying the deposition rate, we control the formation or suppression of an initial tellurium-deficient non-van der Waals phase (Fe3Ge2) prior to realizing epitaxial growth of the vdW FGT phase. Using cross-sectional scanning transmission electron microscopy and scanning tunneling microscopy, we optimize the FGT films to have atomically smooth surfaces and abrupt interfaces with the Ge(111) substrate. The magnetic properties of our high quality material are confirmed through magneto-optic, magnetotransport, and spin-polarized STM studies. Importantly, this demonstrates how the interplay of energetics and kinetics can help tune the re-evaporation rate of chalcogen atoms and interdiffusion from the underlayer. Utilizing these insights, we have developed the growth of FGT and CGT on Bi_2Te_3 for the integration of 2D magnets with TIs.

11:00am **MI+2D+TF-ThM-10 Hybrid Superconductor-Semiconductor Device*, Sergey Frolov,*** University of Pittsburgh **INVITED**

Research into the generation, confirmation and manipulation of Majorana zero modes has brought heightened interest to hybrid materials systems made of fairly conventional components such as s-wave superconductor metals and semiconductors. The game in this arena is to carefully tailor the properties of an electronic device to make possible the observation of exotic physics such as topological superconductivity. The main lesson that we have learned is that the path to any plausible discovery lies through painstakingly careful and very deep understanding of the materials properties and device fabrication conditions. This being true for such a standard set of materials, the lesson certainly applies to more exotic compounds.

In this talk I will briefly summarize the status of the search for Majorana modes in superconductor-semiconductor hybrid devices. I will also highlight other unusual phenomena that arise in these systems such as higher order Josephson effects, time-reversal symmetry broken Josephson current phase relations. I will also show how these materials can be used to build quantum circuits with enhanced functionality, not necessarily arising from topological protection.

11:40am **MI+2D+TF-ThM-12 Magnetotransport in Graphene/$Pb_{0.24}Sn_{0.76}Te$ Heterostructures: Finding a Way to Avoid Catastrophe***, G. Stephen,* Laboratory for Physical Sciences*; I. Naumov,* Howard University*; N. Blumenschein, L. Sun, **Jennifer DeMell,*** Laboratory for Physical Sciences*; S. Shirodkar, P. Dev,* Howard University*; P. Taylor,* Army Research Laboratory*; J. Robinson, P. Campbell,* Naval Research Laboratory*; A. Hanbicki, A. Friedman,* Laboratory for Physical Sciences

While heterostructures are ubiquitous tools to enable new physics and device functionalities, the palette of available materials has never been richer. Combinations of two emerging material classes, 2D materials and topological materials, are particularly promising because of the wide range of possible permutations that are easily accessible. Individually, both graphene and $Pb_{0.24}Sn_{0.76}Te$ (PST) are widely investigated for spintronic applications because graphene's high carrier mobility and PST's topologically protected surface states are attractive platforms for spin transport. Here, we combine monolayer graphene with PST and demonstrate a hybrid system with properties enhanced relative to the constituent parts. Using magnetotransport measurements, we find carrier mobilities up to 20,000 cm^2/Vs and a magnetoresistance approaching 100%, greater than either material alone. We also establish there are two distinct transport channels and determine a lower bound on the spin relaxation time of 4.5 ps. The results can be explained using the polar catastrophe model, whereby a high mobility interface state results from a reconfiguration of charge due to a polar/non-polar interface interaction. Our results suggest that proximity induced interfaces states with hybrid properties can be added to the still growing list of remarkable behaviors in these novel materials.

Advanced Surface Engineering Division
Room 317 - Session SE+AS+BI+SS+TF-ThM

Nanostructured and Multifunctional Thin Films and Coatings I

Moderators: Suneel Kodambaka, University of California Los Angeles, **Jianliang Lin**, Southwest Research Institute

8:00am **SE+AS+BI+SS+TF-ThM-1 Nanostructured Optical Thin Films for Energy Applications and More*, Bill Baloukas,*** Polytechnique Montréal, Canada **INVITED**

The range of applications of optical coatings is ever expanding, and the list of requirements they must fulfil, be it in terms of performance and in terms of functionality, is also increasing. This has stimulated the need for thin film materials with novel nanostructures often based on unconventional materials. The present talk will focus on various coating systems for applications ranging from antireflective (AR) coatings to plasmonic

nanocomposites to passive and active materials for anticounterfeiting, smart windows and micro/nanosatellites.

AR coatings are the most widely implemented optical coating solution as they can be found on ophthalmic and camera lenses, displays, solar cells, etc. Most often based on dielectric materials, their mechanical performance can often be problematic when implemented onto polymer substrates, the latter possessing much higher thermal expansion coefficients. As a means of improving their elastoplastic properties, hybrid films consisting of a combination of organic and inorganic materials were explored. We will also show how this concept was pushed further by producing ultralow refractive index hybrid films by glancing angle deposition (GLAD).

GLAD films have also found application in angular selective coatings, which display anisotropic optical properties. Typically based on metals, we show how the angular selectivity (AS) can be tuned independently from the thickness of the film by conformally overcoating dielectric GLAD films with an absorbing film (e.g.: TiN) deposited by atomic layer deposition (ALD).

While the previous examples are based on passive materials, we have also extensively studied active materials, mainly electrochromic (EC) WO_3 and thermochromic (TC) VO_2. We will discuss how by tuning the deposition conditions, one can deposit, for instance, electrochromic interference filters and highly durable EC films when in the presence of significant ion bombardment. In the case of TC VO_2 films, we will show how, by incorporating them into judiciously designed optical filters, one can enhance their overall optical performance (e.g.: luminous transmittance, solar transmission variation, emissivity change, etc.).

Finally, we will conclude this talk by discussing our most recent implementation of a gas aggregation cluster source to produce various nanoparticles of interest for the above-mentioned optical applications.

8:40am **SE+AS+BI+SS+TF-ThM-3 Constitution, Microstructure and Mechanical Properties of Magnetron Sputtered RuAl Thin Films***, **Vincent Ott**,* Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM), Germany*; T. Wojcik,* TU Wien, Austria*; S. Ulrich,* Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM), Germany*; S. Kolozsvári,* Plansee Composite Materials GmbH , Germany*; P. Polcik,* Plansee Composite Materials GmbH, Germany*; P. Mayrhofer, H. Riedl,* TU Wien, Austria*; M. Stueber,* Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM), Germany

Considering high temperature applications, aluminide intermetallics arrived increasing importance over the last decades. They are well known for their mechanical properties, such as high melting point, strength and good oxidation resistance. In Ni-superalloys, for example, aluminide precipitations are widely used as toughening phase, increasing the high temperature strength and durability of the construction material. Although they are commonly used as an additive in composite materials, their usage as a bulk material is hindered by their poor manufacturing due to its brittle behavior at room temperature.

A relatively new candidate material of B2 structured aluminides is the RuAl intermetallic phase. Compared to other candidates of its class, such as NiAl or TiAl, RuAl exhibits a ductile-brittle-transition below room temperature, which may considerably expand the range of its potential applications.

Thin film synthesis can enable the exploitation of their full potential for example as a protective coating in aircraft and aerospace applications. To elucidate this potential, RuAl single layer thin films were synthesized by magnetron sputtering, utilizing a powder manufactured sputtering target with a composition of 50 at. % Ru and 50 at. % Al. Thin film deposition was done for a variation of the process parameters such as the mode of the power supply, gas pressure and substrate bias voltage to investigate their impact on the thin films constitution and microstructure. Major structural thin film characterization was done by X-ray diffraction and transmission electron microscopy methods. These data are subsequently used to discuss the mechanical properties of the thin films, determined by microindentation.

9:00am **SE+AS+BI+SS+TF-ThM-4 Microstructure, Thermal Stability and Oxidation Resistance of an arc-evaporated $Cr_{0.74}Ta_{0.26}N$ Coating***, **Christina Kainz**,* Christian Doppler Laboratory for Advanced Coated Cutting Tools at the Department of Materials Science, Montanuniversität Leoben, Austria*; M. Tkadletz, M. Burtscher,* Department of Materials Science, Montanuniversität Leoben, Austria*; C. Saringer,* Christian Doppler Laboratory for Advanced Coated Cutting Tools at the Department of Materials Science, Montanuniversität Leoben, Austria*; A. Stark, N. Schell,* Institute of Materials Physics, Helmholtz-Zentrum Hereon, Germany*; C. Czettl, M. Pohler,* CERATIZIT Austria GmbH, Austria*; D. Kiener,* Department of Materials Science, Montanuniversität Leoben, Austria*; N. Schalk,* Christian Doppler Laboratory for Advanced Coated Cutting Tools at the Department of Materials Science, Montanuniversität Leoben, Austria

CrTaN coatings have recently received increasing industrial interest due to their combination of high hardness, beneficial fracture toughness and promising performance in cutting tests. However, up to now, no thorough investigation on the thermal stability and oxidation resistance of this coating system is available. Thus, this work aims to elucidate the evolution of the microstructure and phase composition of an arc evaporated $Cr_{0.74}Ta_{0.26}N$ coating in protective atmosphere and air up to 1400 °C. The as–deposited coating crystallizes in an fcc–$Cr_{0.74}Ta_{0.26}N$ solid solution with a preferred <311> orientation. Alternating Cr–enriched and Ta–enriched nano–layers are identified in the cross–section, which arise from the three–fold rotation during deposition. $Cr_{0.74}Ta_{0.26}N$ powder is stable in protective atmosphere up to temperatures of ~1200 °C, where a transformation into fcc-$Cr_{0.74}Ta_{0.26}N$ to t–$Cr_{1.2}Ta_{0.8}N$ sets in. Vacuum annealing of $Cr_{0.74}Ta_{0.26}N$ on sapphire substrate results in the loss of the nano-layers at 1000 °C, a texture change to <200> at 1270 °C and the transformation to t-$Cr_{1.2}Ta_{0.8}N$ at 1300 °C. When exposed to ambient atmosphere, powdered CrTaN starts to oxidize to t–$CrTaO_4$ and r–Cr_2O_3 at 1050 °C. A partly oxidized CrTaN coating on sapphire was found to consist of intact fcc-$Cr_{0.74}Ta_{0.26}N$ grains close to the substrate interface, a porous transition layer of r-Cr_2O_3 and t-$CrTaO_4$ and a dense r-Cr_2O_3 layer at the surface. The present study confirms the exceptional thermal stability and oxidation resistance of CrTaN coatings, making them promising candidates for use in demanding machining applications.

9:20am **SE+AS+BI+SS+TF-ThM-5 Microstructural Characterization and Tribological Evaluation of TiN, CrN, TiSiCN, and CrSiCN Coatings for Applications in Cold Regions***, **Nicholas D'Attilio**, F. Thompson, G. Crawford,* South Dakota School of Mines and Technology*; E. Asenath-Smith,* US Army Corps of Engineers Cold Regions Research and Engineering Laboratory

Transition metal nitride and nanocomposite coatings have the potential to improve the efficiency, service lifetime, and durability of equipment operating in the extremely cold and dry environments found in Earth's polar regions. Ceramic coatings are sensitive to their operating conditions, and development efforts have been focused on ambient and high temperature environments. Thus, there is a need to understand the influence of arctic conditions on the performance of these materials. To investigate the influence of coating phase content on cold environment performance, TiN, CrN, TiSiCN, and CrSiCN coatings were deposited by plasma enhanced reactive magnetron sputtering. The structure and composition of the coatings was characterized by scanning electron microscopy, energy dispersive X-ray spectroscopy, atomic force microscopy, and X-ray diffraction. Tilting base contact angle goniometry was used to determine the surface energy using the Owens-Wendt-Rabel-Kaelble method. Coating hardness and apparent elastic modulus were measured by nanoindentation. Sliding wear tests were conducted under simulated arctic conditions with a ball-on-flat tribometer equipped with an active cooling stage. Coating microstructure, surface properties, and their relationships to the wear mechanisms identified at low temperatures are discussed.

9:40am **SE+AS+BI+SS+TF-ThM-6 Development and Evaluation of TiAlNb/YSZ Protective Coatings for Titanium Alloys***, **Jianliang Lin**,* Southwest Research Institute, San Antonio Texas*; T. Stinnett,* Lockheed Martin Missiles and Fire Control

There are increasing demands in the development of advanced thermal protection coatings for aerospace components made by titanium alloys for hypersonic applications. A conventional thermal barrier coating based on MCrAlY/YSZ produced by thermal spray or EB-PVD (Electron Beam Physical Vapor Deposition) provided thermal protection, but was found insufficient in thermal stain tolerance and mechanical strength match for titanium alloys. In this study, TiAlNb alloy with specific chemistry was selected as the bond coat for Ti-6Al-4V alloys. The TiAlNb bond coats were prepared by different magnetron sputtering techniques, including plasma enhanced

magnetron sputtering (PEMS), high power impulse magnetron sputtering (HiPIMS), and a combination of PEMS and HiPIMS. The structure, adhesion, oxidation resistance, and thermal fatigue resistance of the TiAlNb coatings was studied by different means. Then an yttrium stabilized zirconium oxide (YSZ) top coat was applied on the top of the optimized TiAlNb by thermal spray. The thermal strain resistance and phase stability of the overall coating system were evaluated using high energy laser irradiation and compared to a thermal spray MCrAlY/YSZ coating in ambient air. It is found that TiAlNb/YSZ outperform MCrAlY/YSZ in high energy laser irradiation, and exhibited no structure and integrity degradation.

11:00am **SE+AS+BI+SS+TF-ThM-10 Imperfections in Metal Diborides – from Ab-Inito Calculations to Transmission Electron Microscopy***, **Martin Dahlqvist**,* IFM, Linköping University, Sweden*; M. Dahlqvist,* Linköping University, Sweden **INVITED**

Transition metal diborides (*M*B_2) are considered as an extremely hard ceramics owing to their outstanding chemical, mechanical, corrosion, thermal and electrical properties. This makes *M*B_2 coatings attractive for applications in erosive, abrasive, corrosive, and high-temperature environments [1]. Typical coatings are overstoichiometric in boron (B/*M*>2) [2] but the recent addition of understoichometic *M*B_2 coatings (B/*M*<2) have widened their compositional range [3-8]. However, when comparing calculated and measured lattice parameters of *M*B_2, perfect match is found for *M* from Group 3 (Sc, Y) and 4 (Ti, Zr, Hf) while deviations are found for *M* from Group 5 (V, Nb, Ta) and 6 (Cr, Mo, W). Reason for this have been discussed to be attributed to non-stoichiometric *M*B_2. In our quest for improving the properties of *M*B_2 we must thus not only master their composition but also related defects. Reliable theoretical studies thus require detailed information about type of defects and their distribution in *M*B_2. It will be shown how theory can be used to identify possible defects in MB_2 and explain the discrepancy between theory and experiment. It will be demonstrated that vacancies in *M*B_2 have a significant impact for *M* from Group 5 (Nb, Ta) and 6 (Mo, W) with improved thermodynamical and dynamical stability as well as mechanical properties. Moreover, extended planar defects have also been identified for multiple *M*B_2 where atomically resolved aberration-corrected scanning transmission electron microscopy imaging, electron energy loss spectroscopy elemental mapping and first principles calculations have been applied to decode the atomic arrangements of the observed planar defects in non-stoichiometric *M*B_2 coatings.

[1] M. Magnuson, et al, Vacuum. **196**, 110567 (2021).
[2] P.H. Mayrhofer, et al, Appl. Phys. Lett. **86**, 3 (2005).
[3] I. Petrov, et al,J. Vac. Sci. Technol. A. **35**, 050601 (2017).
[4] N. Hellgren, et al, Vacuum. **169**, 108884 (2019).
[5] J. Thörnberg, et al, Surf. Coat. Technol. **404**, 126537 (2020).
[6] M.M. Dorri, et al, Scripta Mater. **200**, 113915 (2021).
[7] B. Paul, et al., Acta Mater., **211**, 116857 (2021).
[8] J. Palisaitis, et al, Acta Mater. **204**, 116510 (2021).

11:40am **SE+AS+BI+SS+TF-ThM-12 Mechanical Property and Corrosion Resistance Evaluation of $Ti_xZrNbTaFeB_y$ High Entropy Alloy Thin Films***, B. Lou,* Chang Gung University, Taiwan*; F. Kan,* Ming Chi University of Technology, Taiwan*; **Jyh-Wei Lee**,* Ming Chi University of Technology, Taiwan

High entropy alloy (HEA) thin films have been widely explored due to their unique properties as compared with conventional alloy coatings. In this work, an equimolar TiZrNbTaFe HEA target and a TiB2 target were used to fabricate five TixZrNbTaFeBy HEA thin films with different Ti and B contents using a hybrid high power impulse magnetron sputtering and radio frequency power deposition system. The Ti and B contents were increased by decreasing the input power of TiZrNbTaFe HEA target. The (Ti+B)/(Zr+Ta+Nb+Fe) ratio of the thin films increased from 2.70 to 19.44 as the ZrTiNbTaFe HEA target input power decreased from 200 to 50 W. The TixZrNbTaFeBy thin film kept its amorphous structure while the (Ti+B)/(Zr+Ta+Nb+Fe) ratio was less than 19.44. A nanocomposite microstructure consisting of TiB_2 nanocrystallites embedded in an amorphous TiZrNbTaFe matrix was obtained for the $Ti_{26.4}Zr_{1.1}Nb_{1.0}Ta_{1.3}Fe_{1.1}B_{61.1}$ thin film. The hardness of TixZrNbTaFeBy thin films increased with increasing Ti and B contents. Good adhesion properties were found for five thin films. Each amorphous TixZrNbTaFeBy thin film enhanced the corrosion resistance of bare 304 stainless steel substrate because of the dense microstructures to block the attack of corrosive electrolytes. The amorphous structured $Ti_{26.9}Zr_{3.5}Nb_{3.4}Ta_{3.8}Fe_{3.7}B_{54.6}$ thin film coating exhibited a potential application as a protective coating in harsh environments due to its high hardness of 18.8 GPa, excellent adhesion, good wear resistance, and adequate anticorrosion property.

12:00pm **SE+AS+BI+SS+TF-ThM-13 Tuning the Properties of Thin Films via Disorder***, **Alessandro Troglia**, M. van de Poll,* Advanced Research Center for Nanolithography (ARCNL), Netherlands*; J. van de Groep, A. de Visser,* Van der Waals-Zeeman Institute, University of Amsterdam, Netherlands*; R. Bliem,* Advanced Research Center for Nanolithography (ARCNL), Netherlands

Structural disorder in thin films is often considered detrimental compared to the well-defined nature of epitaxial layers. However, some examples of amorphous thin films show superior properties such as better corrosion resistance, mechanical strength and catalytic performance. Structural disorder can thus serve as an ideal parameter to tune the properties of thin films to specific applications. In this work, we investigate how structural disorder affects the properties of metallic thin films for two selected alloys: CuZr and HfMoNbTiZr. Due to its excellent glass-forming ability, CuZr is an ideal model system for metallic glasses, while the refractory high-entropy alloy (HEA) HfMoNbTiZr has shown a strong preference towards crystallinity. For both materials, amorphous and crystalline alloy thin films of identical composition were achieved by varying the substrate temperature during deposition onto sapphire substrates via pulsed laser deposition (PLD). Grazing-incidence x-ray diffraction (GI-XRD) demonstrate that CuZr thin films grown at room temperature are fully amorphous, while signs of polycrystallinity are observed at 500°C. The effect of disorder is clearly visible in the optical, transport and corrosion properties. The amorphous films are optically transparent in the visible, while polycrystalline films are dark and reflective. The temperature-dependent electronic transport changes its mode from a bad metal to a charge-hopping conductor with an increase in structural disorder. Moreover, the surface chemical properties measured with x-ray photoelectron spectroscopy (XPS) show a clear preference in the surface oxidation of the Cu species. Cu is fully metallic in the disordered film after air-exposure, whereas both oxide and hydroxide species are detected in the polycrystalline film. On the other hand, HfMoNbTiZr thin films grown with PLD are amorphous according to GI-XRD and display a remarkable thermal stability. In contrast with literature, no sign of crystallinity is detected with GI-XRD from room temperature up to 700°C. A further increase of the growth temperature reveals the onset of directed crystallization at 900°C. These results pave the way to the synthesis of metallic thin films with superior and tunable properties via disorder for a wide variety of technological applications.

Thin Films Division
Room 316 - Session TF+AP-ThM

Novel ALD CVD Precursors, Processes, Deposited Morphologies and Substrate Architectures

Moderators: Parag Banerjee, University of Central Florida, **Richard Vanfleet**, Brigham Young University

11:00am **TF+AP-ThM-10 The Electrical and Magnetic Properties of Nonstoichiometric Nickel Oxide Thin Films***, **Mari Napari**,* University of Southampton, UK **INVITED**

Nonstoichiometric nickel oxide (NiO_x), a p-type oxide semiconductor, has gained significant attention due to its versatile and tunable properties. It has become one of the critical materials in wide range of electronics applications and highly sensitive and selective sensors. In addition, the wide band gap and high work function, coupled with the low electron affinity, have made NiO_x widely used in emerging optoelectronics and p-n heterojunctions [1,2]. Also, it is a commonly applied material in heterogenous catalysis. The properties of NiO_x thin films depend strongly on the deposition method and conditions. Efficient implementation of NiO_x in next-generation devices will require controllable growth and processing methods that can tailor the physical, electronic, and magnetic properties of the material.

In this presentation I discuss our work that links together the fundamental electronic properties of NiO_x thin films with the chemical processing methods, and how these can be used in device applications. I discuss how the p-type nature of NiO_x arises and how its stoichiometry affects its electronic properties, and present results that show how the antiferromagnetic nature of the NiO prevails also in the non-stoichiometric films. I will present examples of NiO_x thin films grown by the chemical deposition techniques, including CVD, ALD, and solution processing

approaches, and show how these films can successfully be used in a range of devices and applications, including perovskite solar cells and photoelectrocatalysis [3,4].

[1] Napari et al. "Antiferromagnetism and p-type conductivity of nonstoichiometric nickel oxide thin films" InfoMat 2 (2020) 769-774

[2] Napari et al. "Nickel oxide thin films grown by chemical deposition techniques: Potential and challenges in next-generation rigid and flexible device applications" InfoMat 3 (2021) 536-576

[3] Zhao et al. "In Situ Atmospheric Deposition of Ultrasmooth Nickel Oxide for Efficient Perovskite Solar Cells" ACS Appl. Mater. Interfaces 10 (2018) 41849-41854

[4] Innocent et al. "Atomic scale surface modification of TiO_2 3D nano-arrays: plasma enhanced atomic layer deposition of NiO for photocatalysis" Mater. Adv. 2 (2021) 273-279

11:40am **TF+AP-ThM-12 Al_2O_3 Thin Films with Controlled Nanoporosity Prepared by Low Temperature Thermal ALD**, ***Marceline Bonvalot**, S. Hekking,* LTM - MINATEC - CEA/LETI, France*; C. Vallée,* SUNY POLY, Albany

Because Al_2O_3 is a cheap and abundant material with a very high hardness and inertness to numerous chemicals, porous alumina thin films find a great variety of applications as a filtering material of liquids in the food industry, oil and gas industry, pharmaceutical industry and in biotechnologies as well. In this work, we describe an original experimental route, which leads to the production of Al_2O_3 thin films with controlled nanoporosity. The deposition is carried out by thermal ALD with trimethyl aluminum (TMA) as precursor and at low temperatures (between 50°C and 80°C). The process temperature is deliberately set below the precursor temperature window, so that a significant amount of carbon-rich contaminants remain in the produced thin film, due to poor decomposition of the precursor at low thermal energy. An intermediate O_2 plasma step is then inserted within the thermal ALD cycles, which helps for the degassing of these contaminants leaving behind nanoscale porosities within the thin film under growth. The process optimisation will be presented by discussing the impact of incident plasma power and duration on carbon-rich contamination levels. The frequency of the occurence of the O_2 plasma step inserted within the thermal ALD process will also be investigated, and discussed in regards to imperfectly perfect materials strategies.

12:00pm **TF+AP-ThM-13 Thermal ALD Process of NiO Based on Ni(^{t}Bu-MeAMD)$_2$ Precursor**, ***Cristian van Helvoirt**, N. Phung, M. Creatore,* Eindhoven University of Technology, Netherlands

The applications of NiO thin films have increased over the last years, especially in the fields of electrocatalysis for water-splitting [1] and metal halide perovskite photovoltaics [2]. Previously, we reported an ALD-process for NiO based on bis-methylcyclopentadienyl-nickel as precursor and O_2-plasma as the co-reactant [3]. In this contribution, we investigate a thermal ALD process of NiO, with the motivation of expanding the ALD process capabilities on sensitive (e.g. to O_2 plasma) hybrid organic-inorganic chemistry substrates and offering opportunity for NiO process upscaling by spatial ALD, which is generally based on thermal processes.

For the present study, we selected (N,N′-di-tert-butylacetamidinato)Nickel(II) (Ni(^{t}Bu-MeAMD)$_2$) based on the relatively low melting point (87°C) with reasonable vapor pressure, and the availability of the precursor. Although literature addresses several thermal ALD processes of NiO based on Ni(^{t}Bu-MeAMD)$_2$ with reasonable growth rates [4,5], to our best knowledge, no saturation curves have been reported and only hot wall reactors were used so far. The decomposition temperature of the precursor (237°C), can limit the processing temperature, thereby suggesting the application of cold wall reactors. Hence, in this study, we use a cold wall reactor (FlexAL^{TM} MK1 Oxford Instruments).

We report saturation curves using Ni(^{t}Bu-MeAMD)$_2$ as the precursor and H_2O as the co-reactant resulting in a growth per cycle of 0.40-0.80 Å within a temperature window of 50-200°C. The process at ALD saturated condition also yields excellent uniformity (≥92% homogeneity over an 8 inch silicon wafer), with low impurity level in the film (3% C and 1% N), as observed by X-ray photoelectron spectroscopy (XPS). Rutherford backscattering spectroscopy analysis confirms a nearly stoichiometric film of O:Ni = 1.1 (deposition at 150°C). XPS also reveals the presence of oxide and (oxy)hydroxide terminal groups indicating the presence of both Ni^{2+} and Ni^{3+} oxidation states, imparting the p-type character to the film, key for selective hole transport behavior. Moreover, X-Ray diffraction data show a preferred orientation in the (111) direction for the film as opposed to (200) earlier observed in plasma-assisted ALD NiO, and beneficial for the O_2 evolution reaction in water-splitting [1].

1. Chen, *et al.* (2019) *Chem. Eur. J. 25*, 703 – 713
2. Phung, *et al.* (2022) *ACS Appl. Mater. Interfaces 14*, 1, 2166–2176
3. Koushik, *et al.* (2019) *J. Mater. Chem. C7*, 12532–12543
4. Thimsen, *et al.* (2012) *J. Phys. Chem. 116,* 16830−16840
5. Hsu, *et al.* (2015) *Nanotechnology26*(38), 385201

Thin Films Division
Room 316 - Session TF1+SE+SS-ThM

Nucleation, and Interface Phenomena in Thin Films

Moderators: Adrie Mackus, Eindhoven University, Netherlands, **Qing Peng**, University of Alabama

8:00am **TF1+SE+SS-ThM-1 Opportunities of Complex Oxides Prepared by Atomic Layer Depositions**, *P. Sallés, P. Machado,* ***Mariona Coll,*** ICMAB-CSIC, Spain **INVITED**

The rapid development of electronic devices, telecommunication systems, and sensors pushes new functional demands with increasingly stringent requirements like flexibility, light weight, and miniaturization. Transition metal oxides present the richest variety of functional properties due to the large diversity of chemical compositions and structures that they can offer. However, the preparation and manipulation of crystalline yet bendable functional complex oxide membranes has been a long-standing issue as they require specific crystalline substrates and high temperature treatments. We have developed a facile chemical route based on the use of $Sr_3Al_2O_6$(SAO) sacrificial layer to detach oxide thin films of various compositions from the growing substrate and enable their transfer to flexible substrates.[1] Meticulous chemical and structural study of the SAO film have allowed us to identify the formation of an amorphous SAO capping layer and carbonates upon air exposure, which dictate the crystalline quality of the subsequent oxide film growth.[2] Judicious cation substitution in SAO enabled both decreasing reactivity with ambient moisture and modulating the strain state of the subsequent heterostructures grown on it. Upon detailed investigation of oxide adhesion on polymeric substrates and sacrificial etching (figure 1), crystallinity, surface morphology, interface cation diffusion, mechanical and electrical properties of transfer printed heteroepitaxial $BiFeO_3/La_{0.7}Sr_{0.3}MnO_3$ membranes have been studied and compared with rigid substrates. From this work it is envisaged many new opportunities to prepare artificial oxide heterostructures and devices offering a whole new dimension for electronics and beyond.

[1] P. Salles, M. Coll et al. Adv. Funct. Interfaces, 2001643 (2021)

[2] P. Salles, M. Coll et al. ACS Appl. Mater. Interfaces , 14, 10, 12845–12854 (2022)

8:40am **TF1+SE+SS-ThM-3 An Atomic-Scale Study of Si Epitaxial Growth on Cl-Si(100)**, ***Azadeh Farzaneh,*** University of Maryland, College Park*; R. Butera,* Laboratory for Physical Sciences

Atomically-precise fabrication techniques utilize a scanning tunneling microscope to lithographically define electronic devices and components, where a monatomic layer of H or Cl adsorbed on Si(100) acts as a resist. Unlike traditional resists, these monatomic resists either desorb or remain at the growth front during subsequent growth of Si capping layers.While the body of literature extensively explores Si deposition and subsequent diffusion on H-Si(100), Cl-Si(100) has remained relatively unexplored.A detailed understanding of the thin film growth mechanism enables atomic level control of the interface, which starts with diffusion of adatoms in dilute regimes on the surface. Here we explored the initial stages of Si growth on Cl-Si(100) and characterized thin Si films (~25 nm) grown on this surface. The activation energy for Si adatom diffusion on Cl-Si(100) was extracted from STM observations combined with simulations of a simple random walk model rooted in the mechanism of Si chain formation at different temperatures. Ex-situ characterization of thin Si films grown on Cl-Si confirmed the formation of crystalline layers and the near complete removal of Cl from the Si matrix. The epitaxial film obtained on Cl-Si(100) and absence of Cl from the interface confirm Cl as a viable resist for current atomically precise fabrication schemes. This opens up new pathways for introducing new chemistries and materials into the picture.

9:00am **TF1+SE+SS-ThM-4 The Effect of Oxygen Plasma on the ZnO Growth on Polymer Substrates During Plasma-Enhanced Atomic Layer Deposition**, ***Lisanne Demelius,*** Graz University of Technology, Austria; *M. Blatnik,* CEITEC – Central European Institute of Technology, Brno University of Technology, Czechia; *K. Unger,* Graz University of Technology, Austria; *P. Parlanti, M. Gemmi,* Istituto Italiano di Tecnologia, Center for Materials Interfaces, Italy; *A. Coclite,* Graz University of Technology, Austria

Atomic layer deposition (ALD) is a powerful technique to deposit highly conformal thin films the thickness of which can be precisely controlled. However, the use of polymeric substrates often leads to non-ideal ALD processes that result in precursor diffusion and subsurface growth of the deposited material.
Plasma-enhanced ALD (PE-ALD) is known to enhance nucleation due to the surface-activating effect of plasma and can be expected to significantly reduce subsurface diffusion, enabling the surface-limited deposition of thin conformal coatings. However, plasma can also have detrimental effects on polymeric substrates.

Our work contributes to a deeper understanding of how oxygen plasma applied during PE-ALD affects film formation, nucleation, and interface formation of ZnO on polymer substrates. In-situ spectroscopic ellipsometry was used as the main technique to monitor the PE-ALD growth of ZnO on selected polymer thin films. To better understand how the chemical structure of the polymer influences plasma-substrate interactions and ZnO thin film formation, both crosslinked and linear polymers exhibiting varying degrees of reactivity with the ALD precursor were studied.

Our results show that while the plasma efficiently activates the polymer surface to enable rapid ZnO nucleation, it can also cause significant substrate etching that dominates the initial stage of growth until, at a certain point, ZnO growth takes over and the regime of normal ALD growth behavior is entered. The strength and extent of etching strongly depends on the type of polymer. Despite the initial etching, the resulting thin films exhibit sharp interfaces and a quality, in terms of surface roughness, crystallinity and ZnO density, comparable to those of ZnO deposited on silicon.

A closer examination of the first 25 PE-ALD cycles showed that, on the nanometer scale, the simultaneous etching of the polymer and ZnO nucleation leads to a certain degree of intermixing at the interfaces, the extent of which depends on the type of polymer. It was also revealed that, during the first few cycles, no stochiometric ZnO is yet formed but instead Zinc is found to be bonded to hydroxyl groups and presumably oxygen-carbon species from the polymer, forming hybrid bonds. This points to a strong interaction between the polymer substrate and the forming ZnO, which can be expected to result in good film adhesion, a property that is critical in all applications involving mechanical stress and strain.

9:20am **TF1+SE+SS-ThM-5 Measuring Local Atomic Structure Variations Through the Depth of Ultrathin ALD Aluminum Oxide**, ***Nikhila Paranamana***, *M. Young, R. Gettler, H. Koenig, S. Montgomery-Smith, X. He,* University of Missouri, Columbia

Understanding the atomic structure of ultrathin (<20 nm) atomic layer deposition (ALD) coatings is critical to establish structure property relationships and accelerate the application of ALD films to address technological needs. Previous studies have measured the atomic structure of nanoscale ALD films using cryogenic electron diffraction with a large (~200 nm) beam diameter. However, for ultrathin ALD coatings, these measurements provide only ensemble average structural information and cannot be used to directly measure differences in atomic structure through the depth of the ALD film. In this study, we localize the electron beam to a small (~ 5 nm) spot size using cryogenic scanning transmission electron microscope (STEM) and we collect electron diffraction data at multiple points along the depth of a 12 nm thick ALD AlO_x film deposited onto a CNT substrate without a contribution from the substrate. We couple these diffraction measurements with pair distribution function (PDF) analysis and iterative reverse Monte Carlo-molecular statics (RMC-MS) modeling to compare atomic structure metrics at different positions in the film depth. We interpret the modeling results considering the 3D concentric cylindrical sample geometry of a CNT with uniform AlO_x coating. These measurements confirm a two-phase bulk/interface structural model proposed previously for ALD AlO_x, and indicate that the interfacial layer at the CNT-AlO_x interface is 2.5 nm thick – five times larger than previously reported. This report demonstrates direct measurement of atomic structural variations across ultrathin films that is of broad interest for understanding local differences in atomic structure across material interfaces.

9:40am **TF1+SE+SS-ThM-6 Interfacial Reactions and Energy Transfer in Sputter Deposited Thermite Reactive Nanolaminates**, ***Chloe Skidmore,*** *J. Maria,* Pennsylvania State University

Cost effective energetic materials with highly tunable ignition and actuation have important applications in both military and commercial sectors. Recently, interest has grown in nanoenergetic composites due to their potential as stand-alone explosives with greater reliability, heat release, and combustion efficiency. Thermite is a versatile inorganic energetic of specific significance due to the highly exothermic reduction-oxidation reaction that occurs between metal and oxide constituents, resulting in self-sustaining heat production. However, if the high energy release and improved tunability provided by the diverse chemistries of inorganic energetics is to be utilized, a fundamental understanding of the initiation and propagation processes in new nanoenergetic materials such as thermite is necessary. Thin film deposition of multilayered stacks of alternating metallic and oxide layers with well defined interfaces offers a streamlined process to observe energy transduction and the chemical reactions that mitigate interface reactions. These multilayered stacks, termed reactive nanolaminates (RNLs), facilitate control over reactant thickness, diffusion distance, interface quality and the total material involved, while also reducing premature intermixing of metal and oxide layers. This presentation explores energy release in sputter deposited CuO-Mg RNLs as a function of bilayer thickness, plasma energetics, and metal-oxide layering sequence. These samples are analyzed via in-situ high temperature x-ray diffraction (XRD) and differential scanning calorimetry (DSC), as both probe the oxygen exchange process by structure evolution and energy production, respectively. The bulk properties associated with the Mg-CuO thermite system suggests extensive oxygen dissolution in the starting metal and the possibility of transient eutectic liquid formation during reaction. XRD results indicate that CuO/Mg RNLs exhibit eutectic liquid formation during reaction, with Cu_xMg_yintermetallics temporarily appearing around 565°C. DSC analysis reveals exotherm maxima at temperatures associated with critical points in the Mg-Cu phase diagram. More precisely, as interfacial area is increased the max exothermic peak shifts from ~650°C (T_m Mg) to ~565°C (T_m Mg_2Cu) before finally occurring at ~483°C (T_m eutectic Mg/Mg_2Cu). Preliminary DSC analysis also suggests that, relatively speaking, sputtering energetics resulting in smoother, more crystalline Mg interlayers, shifts the maximum exothermic peak to higher temperatures. These findings provide insight into the mechanisms of energy transfer in thermite RNLs, allowing for highly tunable, reliable energetic materials.

Applied Surface Science Division
Room 320 - Session AS+2D+EM+MS+NS+SS+TF-ThA

Probing Defects at Surfaces and Interfaces

Moderators: Michaeleen Pacholski, The Dow Chemical Company, **Zachary Robinson**, SUNY Brockport

2:20pm **AS+2D+EM+MS+NS+SS+TF-ThA-1 Controlling InP Quantum Dot Surface Defects Using ALD-inspired Surface Chemistry and Phosphorus Kα and Kβ X-ray Emission Spectroscopy***, Nayon Park,* University of Washington **INVITED**

Colloidal InP quantum dots are a leading heavy-metal-free semiconductor material for spectral downconversion in current generation display technologies and future generation energy efficient LEDs. Achieving the brightest and narrowest photoluminescence (PL) relies on the synthesis of structurally and electronically defect-free quantum dots. InP quantum dots' high propensity for oxidation and the inherent oxidative defects arising from commonly used synthesis methods therefore motivates a systematic approach to probe InP oxidation as a function of synthesis and surface treatments and correlation with the resultant optical properties. Phosphorus X-ray Emission Spectroscopy (XES) presents itself as an exceptional tool in this regard. In this talk, I will show recent results from computational modeling where we find that native InP surface oxides give rise to dark states near the band edge. Replacing the surface indium with zinc to form a monolayer ZnO shell results in the reduction of dark states. Using ALD-inspired successive ionic layer adsorption and reaction (SILAR), we developed the colloidal, layer-by-layer growth strategy of metal oxide shells (i.e. ZnO, CdO, GaO_x, AlO_x) on InP quantum dots at room temperature using common ALD precursors (*i.e.*, metal alkyls and water). Metal oxide-shelled InP QDs generally show enhanced PL and evidence of bulk and local structural perturbations arising from the metal oxide as determined by X-ray diffraction and X-ray absorption spectroscopy. Further, we explore the impact of these metal oxide interfaces on the PL QY and emission linewidth of InP/ZnSe core/shell QDs. Upon growing a thin ZnSe shell, we observe improved PL properties, which we hypothesize to be attributable to the inhibition of phosphorus migration to the shell due to the presence of the metal oxide interlayer, as supported by X-ray emission spectroscopy. Taken together, these results suggest a clear path forward in the control and design of complex QD interfaces with atomistic insight for optoelectronic technologies.

3:00pm **AS+2D+EM+MS+NS+SS+TF-ThA-3 Characterization of MAX Phases using a Combination of Micro-spot XPS, HAXPES and C60 Cluster Depth Profiling***, **Kateryna Artyushkova**,* Physical Electronics USA*; M. Anayee, Y. Gogotsi,* Drexel University

Two-dimensional (2D) transition metal carbides, carbonitrides, and nitrides (MXenes) have seen significant increases in the number of research areas and publications. MXenes have a unique combination of properties that have led to many applications.[1] MXenes are usually synthesized by etching "A" layers that interleave "MX" layers in the bulk MAX precursors. MAX are represented by Mn+1AXn, where M denotes early transition-metals (Ti, V, Cr, Mo, etc.), X is N or C, and A is an A-group element such as Al, Si and others. During synthesis, impurities and defects may be introduced, which significantly impact the properties of the resulting materials. It is therefore critical to detect and quantify these defects and impurities.

X-ray Photoelectron Spectroscopy (XPS) has the advantages of being easily quantifiable and providing chemical information such as surface termination and oxidation. However, there are many challenges in using XPS for analyzing MAX and Mxene. The first is a very small size of MAX, less than a few tens of microns. With the development of focused scanning micro-probe X-rays, these limitations can be overcome. The other challenge is the extreme surface sensitivity of XPS. It is challenging to separate surface adventitious carbon and oxygen from possible oxygen incorporation in the carbon site. Depth profiling using a monatomic Ar ion beam is not suitable as it can introduce damage to the structure of MAX.

In this work, we are presenting two approaches to address this challenge. The first involves the application of Hard X-ray Photoelectron Spectroscopy (HAXPES), in which a monochromated Cr X-ray source is used to probe ~3 times deeper than a soft Al X-ray. The second utilizes a cluster ion gun source, such as C60, for damage-free depth profiling through individual MAX particles using ~8µm X-ray spot for probing if oxygen is present in the MAX structure.

3:20pm **AS+2D+EM+MS+NS+SS+TF-ThA-4 Unusual Trend in Thermal Stability of Alanine Different Ni Surfaces***, J. Ontaneda,* Queen Mary University of London, UK*; R. Grau-Crespo,* University of Reading, UK*; **Georg Held**,* Diamond Light Source, UK

Chirally modified heterogeneous catalysts promise massive savings of cost and toxic waste in the production of enantiopure precursors for high-value chemicals such as pharmaceuticals, fertilizers, or fragrants [1]. A key aspect is the thermal stability of chiral modifiers, which generally are chiral organic molecules bound to a chemically active metal surface. The enantioselective hydrogenation of methylacteoacteate (MAA) is a topical reaction, which is catalysed by nickel modified with chiral carboxylic acids, such as alanine, tartaric acid, or aspartic acid [2]. The components of this catalytic system have been investigated using various surface sensitive techniques [3,4,5]. Here we present a study of the thermal stability of alanine on the three most common Ni surfaces, {111}, {100}, and {110}, using synchrotron-based temperature-programmed photoelectron spectroscopy and X-ray absorption spectroscopy. In contrast to common experience with smaller molecules, alanine is more stable on the more open {110} and {100} surfaces compared to {111}. Comparison with a detailed DFT study identifies structural and electronic effects that play a role in this unusual behaviour.

References:

[1] G. Held and M. J. Gladys, Topics in Catalysis 48 (2008) 128 – 136.
[2] Izumi, Y., Adv. Catal. 1983, 32, 215−271.
[3] Keane, M. A., Langmuir 1994, 10, 4560−4565.
[4] P. Tsaousis, et al., J. Phys. Chem. C 122 (11) (2018) 6186 – 6194.
[5] R. E. J. Nicklin, et al., J. Phys. Chem. C 122 (2018) 7720 – 7730.
[6] W. Quevedo, et al., Langmuir 36 (2020) 9399 – 9411.

3:40pm **AS+2D+EM+MS+NS+SS+TF-ThA-5 Correlative Theoretical and Experimental Study of the PC | X Interfacial Bond Formation (X = TiN, AlN, TiAlN) During DC Magnetron Sputtering***, **Lena Patterer**, P. Ondračka, D. Bogdanovski, S. Karimi Aghda, J. Schneider,* Materials Chemistry, RWTH Aachen University, Germany

Due to their outstanding oxidation and wear resistance, cubic (Ti,Al)N is widely used as protective coatings on forming and cutting tools. These characteristics make (Ti,Al)N also an attractive candidate for the protection of polymer components. The composition-induced changes in the interfacial bond formation of DC magnetron sputtered TiN, AlN, and $Ti_{0.25}Al_{0.25}N_{0.5}$ onto polycarbonate (PC) substrates are systematically investigated by correlating theory and experiment. In order to simulate the sputtering condition by *ab initio* molecular dynamics, a periodic structural model of bulk PC consisting of 394 atoms was bombarded by several Ti, Al, and N atoms with a kinetic energy of 1 eV. While both Ti and N atoms show high reactivity towards all functional groups of the polymer during the surface bombardment, Al atoms selectively react only with the carbonate group of PC or other reactive functional groups that have formed during previous bombardment events (e.g. C-N groups). At the PC | TiN and PC | TiAlN interfaces, Ti and N contribute equally to the interfacial bond formation, whereas the PC | AlN interface is defined mostly by C–N groups with Al-rich clusters forming on top of these groups. X–ray photoelectron spectroscopy data of the PC | X interfaces (X = TiN, AlN, TiAlN) show a very good agreement with the above-discussed predictions as the formation of C-N, C-(Ti,Al), and (C–O)–(Ti,Al) bonds is experimentally verified. This shows that the here employed computational strategy enables predictions of the interfacial bond formation between polycarbonate and metal nitrides, and it is reasonable to assume that the here proposed research strategy can be readily adapted to other polymer | inorganic material interfaces.

4:00pm **AS+2D+EM+MS+NS+SS+TF-ThA-6 Using Resonant Photoemission Spectroscopy to Probe the Electronic Structure of Complex Oxides with Elemental and Orbital Specificity***, **Jessica McChesney**, D. Fong, H. Hong,* Argonne National Laboratory, USA

Understanding the role of defects and interfaces is necessary in order to realize many of the promising novel properties of complex oxide heterostructure devices. To this aim, we employ resonant angle-resolved photoemission spectroscopy to probe the electronic structure with elemental and orbital specificity of complex oxide heterostructure $LaTiO_3/SrTiO_3$ (LTO/STO).Combining these spectroscopy measurements with in-situ growth characterization we are able to determine the minimum thickness required to achieve high quality heterostructures with abrupt interfaces and to correlate the formation with the 2DEG with the

interface termination LTO/STO vs STO/LTO.In addition, we explore the role of oxygen vacancies in formation of the 2DEG on the bare substrate and reveal that contrary to expectations, the 2DEG is Ti^{4+} in character while the oxygen defects are Ti^{3+} in character.

Thin Films Division
Room 316 - Session TF+AS-ThA
In-Situ Characterization of Thin Films and Interfaces

Moderators: James Fitz-Gerald, University of Virginia, **Robert Grubbs**, IMEC Belgium

2:20pm **TF+AS-ThA-1 *In situ* IRRAS and XPS for the Characterization of Gas Interactions with MOF Nanofilms***, **Tianhao Hu,*** Stony Brook University/Brookhaven National Laboratory*; C. Eads,* Max IV Laboratory, Sweden*; D. Stacchiola, A. Head,* Brookhaven National Laboratory

The need for novel solid catalysts for use in industry has demanded the development and the application of new techniques of *in situ* spectroscopy which enables the study of catalysts in conditions close to industry. Infrared spectroscopy and X-ray photoelectron spectroscopy (XPS) are complementary techniques that provide chemical and electronic structure information and have been widely used under *in situ* conditions. However, applying these techniques to insulating powders, such as metal-organic frameworks (MOFs), in controlled environments can be challenging. Here we grow films of archetypical MOFs, UiO-66 and UiO-66(NH_2), via a vapor-assisted conversion method and incorporate Pt catalytic sites (Pt@UiO-66(NH_2)) through solution impregnation. Using ambient pressure XPS, the electronic structure of the MOF and the oxidation state changes of the Pt are followed under various gas dosing conditions. Using infrared reflection absorption spectroscopy (IRRAS) and the adsorption of probe molecules N_2, CO, CO_2, and ethylene, under-coordinated metal sites and the acid strength of hydroxyl groups are characterized. IRRAS was also used to follow the oxidation of CO catalyzed by Pt@UiO-66(NH_2). Signature IR bands for gas phase CO_2 product and CO interacting with Pt^0 sites at 2024 cm^{-1} and 2098 cm^{-1} are found. This study highlights the information to be gained by applying traditional surface science techniques to nanoscale films for chemical, electronic, and reactivity characterization.

2:40pm **TF+AS-ThA-2 AVS Nellie Yeoh Whetten Awardee Talk: Characterizing Early-Stage Morphology and Defect Dynamics in Block Copolymer Thin Films with Environmentally Controlled High-Speed Atomic Force Microscopy***, **Julia Murphy**[1],* University of Chicago*; J. Raybin,* University of California at Berkeley*; S. Sibener,* University of Chicago

The spontaneous self-assembly of block copolymers into a variety of nanoscale morphologies makes these systems ideal candidates for next-generation lithography applications. However, industrial application requires long-range control over the domain order and orientation. Extensive work has been done to achieve linearity in nanopatterns on wafer size scales, but there is also a need to control the formation of point defects to generate, for example, T-junctions, jogs, and bends for semiconductor templating applications. As such, a fundamental understanding of block copolymer nanopattern formation and how structural defects contribute to instability in the films is crucial to achieve the perfection required to utilize these thin films as lithographic templates for nanotechnologies. Here, I present recent work on poly(styrene-*block*-methyl methacrylate) (PS-*b*-PMMA) thin films with environmentally controlled high-speed atomic force microscopy (AFM). By imaging films with minor variations in thickness above the glass transition temperature, we capture the early formation of hole, island, and continuous relief structures during thermal annealing. Additionally, we see how the striped nanoscale pattern develops in tandem with the changing mesoscale features. Confining the PS-*b*-PMMA in lithographic templates that are tapered in width, or wedge-shaped, generates dislocations at precise intervals locations in otherwise linearly aligned polymer domains. Examining polymer confined in these films reveals the pathways by which dislocations evolve and annihilate during thermal annealing, and how point defects in nanopatterns influence interfacial fluctuations in the surrounding polymer domains. Together, these studies contribute to the fundamental understanding of the dynamics and ordering of block copolymer thin films and reveal how topography - both native and imposed by lithography – impacts the nanoscale structure.

3:00pm **TF+AS-ThA-3 *In Situ* X-Ray Scattering Studies of the Influence of Plasma Properties on Epitaxial InN Growth by PEALD***, **Jeffrey Woodward**, S. Rosenberg, D. Boris,* U.S. Naval Research Laboratory*; M. Johnson,* Syntek Technologies*; S. Walton, S. Johnson,* U.S. Naval Research Laboratory*; Z. Robinson,* SUNY Brockport*; N. Nepal,* U.S. Naval Research Laboratory*; K. Ludwig,* Boston University*; J. Hite, C. Eddy,* U.S. Naval Research Laboratory

Plasma-enhanced atomic layer deposition (PEALD) enables the epitaxial growth of ultrathin indium nitride (InN) films at significantly reduced temperatures and with atomic-level control of layer thickness. These advantages are challenged by the inherent complexity of the growth process due to the reliance on plasma surface interactions [1], which necessitates a detailed understanding of the relationship between the plasma and the growth kinetics. To this end, synchrotron hard x-ray scattering techniques are well-suited to the *in situ* study of PEALD processes, as they are capable of operating in harsh environments during chemical reactions and can provide real-time information about the structural properties of the film. One such technique, grazing incidence small-angle x-ray scattering (GISAXS), probes nanoscale fluctuations in electron density averaged across the sample, which can provide an in-depth description of surface topography [2]. Initial studies of epitaxial InN growth under fixed plasma conditions demonstrated the utility of GISAXS for understanding the kinetics of PEALD processes, and showed that the growth proceeded in a Stranski-Krastanov mode where the critical thickness for island formation and the coarsening behavior were strongly influenced by temperature [3].

In this work, we utilize *in situ* GISAXS to investigate the early-stage PEALD growth kinetics of epitaxial InN within three different plasma regimes. The GISAXS data are supported by diagnostic studies of the plasma species generation in the inductively coupled plasma source as a function of the relative concentrations of the nitrogen/argon gas mixture used in the growth process. The growth mode is found to be correlated to the production of nitrogen species in the plasma, with high concentrations of atomic N species promoting Volmer-Weber growth and low concentrations promoting Stranski-Krastanov growth. Under conditions of high atomic N production, both the island radius and critical thickness for island formation are found to increase with ion flux. Furthermore, the InN island distance and areal density are found to change only during plasma exposure, and to continue changing with exposure even after the methylindium adlayer is believed to have fully reacted with the plasma. Our results demonstrate the potential to control the growth kinetics during PEALD of epitaxial films by intentionally accessing specific regimes of plasma species generation.

References

[1] D.R. Boris *et al.*, J. Vac. Sci. Technol. A **38**, 040801 (2020)
[2] G. Renaud, R. Lazzari, and F. Leroy, Surf. Sci. Rep. **64**, 255 (2009)
[3] J.M. Woodward *et al.*, J. Vac. Sci. Technol. A **37**, 030901 (2019)

3:20pm **TF+AS-ThA-4 Optical Monitoring of $MoCl_5$ and H_2S Delivery During Atomic Layer Deposition of MoS_2***, **Berc Kalanyan,*** National Institute of Standards and Technology*; E. Jahrman,* National Institute of Standard and Technology*; J. Maslar,* National Institute of Standards and Technology

Low-temperature (<400 °C) deposition of transition metal dichalcogenide (TMD) films has been proposed as a potential route for fabricating diffusion barrier structures in field effect transistors and other electronic devices. Atomic layer deposition (ALD) is well-suited to this application due to its low thermal budget and high conformality, enabling its integration into back-end of line processing. Several publications have described the deposition of layered MoS_2 films by ALD, most commonly using $MoCl_5$ and H_2S as precursors[1–4]. Inorganic precursors may be desirable for their high thermal stability and the lack of organic ligands, which often are a source of impurities in deposited films. However, $MoCl_5$ is a low-volatility solid under typical delivery conditions and can readily form oxychlorides upon exposure to moisture. Delivery challenges associated with $MoCl_5$ are reflected in the large variety of delivery methods and conditions reported in the literature, for instance a vessel temperature range of 70 °C to 210 °C. Deposition studies using $MoCl_5$ and H_2S also show inconsistent results with respect to MoS_2 morphology, grain size, and composition, with no deposition reported under some conditions[5]. This lack of reproducibility could stem from variations in $MoCl_5$ flux observed under different delivery configurations. To address this possibility, we monitored the flow of $MoCl_5$ and H_2S as a function of delivery conditions using direct absorbance measurements. We measured vapor phase spectra of neat $MoCl_5$ and its common oxychlorides using an ultraviolet-visible (UV-vis) spectrometer under static conditions. To evaluate precursor delivery under flow, we

[1] **AVS Nellie Yeoh Whetten Awardee**

implemented in-line gas analyzers each consisting of a broadband source, a filter for wavelength selection, and an avalanche photodiode. We evaluated the delivery rates of $MoCl_5$ and H_2S injected from vapor draw and direct draw vessels, respectively. In addition to vapor phase measurements, we used real-time spectroscopic ellipsometry to characterize precursor adsorption under varying delivery conditions. Using results from these measurements, we will discuss the reproducibility of $MoCl_5$ and H_2S delivery rates and potential implications for MoS_2 deposition.

[1] R. Browning et al., Mater. Res. Express **2**, 035006 (2015).

[2] A. Valdivia et al. Vac. Sci. Technol. Vac. Surf. Films **34**, 021515 (2016).

[3] L. Liu et al., Nanotechnology **28**, 195605 (2017).

[4] W. Ahn et al., Phys. Status Solidi RRL – Rapid Res. Lett. **15**, 2000533 (2021).

[5] M. Mattinen et al., Adv. Mater. Interfaces **4**, 1700123 (2017).

3:40pm **TF+AS-ThA-5 Temperature-Time-Thickness (TTT) Topography Maps: A Parameter Space Visualization Approach for ALD Processes***, **S. Novia Berriel**, C. Feit, U. Kumar,* University of Central Florida*; A. Arunachalam,* University of Texas at Dallas*; S. Seal,* University of Central Florida*; K. Basu,* University of Texas at Dallas*; P. Banerjee,* University of Central Florida

In atomic layer deposition (ALD), an optimized process is characterized by its stability, predictability, and self-limiting nature. Each of these characteristics is quantified individually with separate sets of experiments. For stability, temperature is varied while holding pulse time constant. Similarly, a process's self-limiting nature is determined by saturation curves, varying the pulse time (i.e., dose) of the precursors while holding temperature constant. These data are usually presented in such as way as to imply no interdependency between them. This is a limited view of process optimization that will only yield partial understanding of deposition characteristics. We propose the information held in the interdependencies of these parameters can lead to improved process development and better control of final film properties.

We have used in situ spectroscopic ellipsometry to capture temperature-time-thickness (TTT) topography maps of ALD processes. The TTT contour plots are 3D visualization maps that demarcate dose saturation times, temperature windows, and corresponding growth rates. Based on a methodology recently published by our group[1], we demonstrate TTTs of several thermal ALD processes including CeO_2, Al_2O_3, ZnO, TiO_2, as well as plasma enhanced ALD (PEALD) of TiO_2. These topographies collectively show stability, adsorption, and reaction (i.e., thermodynamic) characteristics of the precursor reactant molecules. TTT curves are also obtained as single-substrate experiments, thus reducing process development times and resource consumption. We propose a comprehensive database of TTT diagrams can be used for improved process development and can eventually provide guidance towards the development of precursors finely tuned to the requirements of ALD processes.

[1]U. Kumar *et al*., "In situ ellipsometry aided rapid ALD process development and parameter space visualization of cerium oxide nanofilms," *J. Vac. Sci. Technol., A*, vol. 39, no. 6, 2021, doi: 10.1116/6.0001329.

4:00pm **TF+AS-ThA-6 Surface Functionalization of Cu with Inhibitors to Enable Area-Selective Atomic Layer Deposition***, **Andrew Kaye**, S. Agarwal,* Colorado School of Mines

Area-selective atomic layer deposition (AS-ALD) is a bottom-up fabrication technique that can address challenges related to conventional lithography in the fabrication of integrated circuits. Cu is the predominant interconnect metal while SiO_2 is used as the dielectric. In this work, we explore the growth of a dielectric on SiO_2, with Cu as the nongrowth surface. Using *in situ* reflection-absorption infrared spectroscopy (RAIRS) we previously showed that thiols are effective inhibitors for Cu, and readily adsorb onto the surface by reducing the native CuO_x layer. However, thiols have a low vapor pressure and thermal stability on Cu. With these inhibitors, the Cu surface can be re-dosed between ALD cycles, which is essential in plasma-assisted ALD processes. Moreover, the inhibitor readily desorbs from the non-growth surface after AS-ALD, which eliminates surface cleaning steps that are normally required with self-assembled monolayers. Recently, several small molecule inhibitors for Cu have been reported in the AS-ALD literature including alkynes, aniline, and pyridine.

For alkynes, we show that a H_2 plasma cleaning step is required to reduce the native CuO_x layer on the Cu surface. When Cu wafers left in atmospheric conditions are exposed to an H_2 plasma, RAIRS shows that surface carbonates are removed, which indirectly confirms the presence of surface CuO_x. Specifically, we show that after we optimized the H_2 plasma cleaning duration at 200 °C, 5-decyne adsorbs on the Cu surface. The adsorption of 5-decyne is apparent from the appearance of –C=C– and –C≡C– stretching vibrations in the ~1600 and ~2200 cm^{-1} regions, respectively. In addition, we also observed the CH_x stretching and bending modes in the ~2900 and ~1400 cm^{-1} regions, respectively. Adsorption of 5-decyne on PVD and CMP Cu was observed over the temperature range of 28 to 150 °C. As the substrate temperature increased for the PVD Cu surface, the intensity of the –C=C– mode decreased while the –C≡C– mode increased, indicating that chemisorption is favored at lower temperatures while strong physisorption is favored at higher temperatures. At higher temperatures, the CH_x stretching and bending mode intensities decreased, indicating lower 5-decyne adsorption. ALD of Al_2O_3 on Cu with 5-decyne as an inhibitor was tested with dimethyl aluminum isopropoxide (DMAI) and H_2O. Even at sub saturation doses of DMAI, AS-ALD was not observed. We will also compare 5-decyne as an inhibitor with aniline and pyridine, which have been demonstrated as more promising candidates.

Thin Films Division
Room Ballroom A - Session TF-ThP
Thin Film Poster Session

TF-ThP-1 Effect of Metallic Bonding on the Optical Properties of Transition Metal Based Thin Films*, Nimarta Kaur Chowdhary*, *T. Gougousi,* UMBC

Combining electronics and photonic devices on a single chip provides a powerful approach to resolving technological issues, from solar technology to low-power computing systems. Next-generation high-speed photonic devices require materials with large and fast optical nonlinearities. Integrating electronic and photonic devices on a single chip has proved challenging due to the limited availability of nonlinear materials compatible with the semiconductor industry process flow. Transition metal oxide thin films may serve as a potential solution to this problem.

It has been shown that atomic layer deposition (ALD)-grown as-deposited TiO_2thin films demonstrated large $n_2$values, which were 4-6 orders larger than previously reported [1]. X-ray photoelectron spectroscopy (XPS) revealed that these TiO_2 films incorporated Ti-O-N/TiN metallic bonds during growth [1]. The very large enhancement that occurred for ALD films grown at 250 °C was a result of about 1 at. % of Ti-O-N bonds evenly distributed within the films [1]. Although silicon and most dielectric materials used in the electronic industry show little to no nonlinear optical response, it is predicted that the addition of metallic impurities in the bulk during the fabrication process will be an optimal way to induce nonlinearities while maintaining compatibility with the process cycle.

We investigated two complementary ways to incorporate metallic bonding starting with either metal oxide (hafnium dioxide, titanium dioxide) or metal (titanium, titanium nitride) thin films. The former is grown using ALD, and to enhance the metallic bonding, we attempted to promote precursor decomposition by using growth parameters such as temperature and purge times outside the optimal ALD window. Metal films were grown by physical vapor deposition (PVD) and post-deposition thermal treatment was used to control the amount of metal bonding. The ALD films showed some metallic bonding that was accompanied by an increased concentration of bonded carbon impurities. This metallic bonding was found to affect the films' bandgap with absorption extending further into the visible than for pure TiO_2 films.

This approach to accomplishing large nonlinearities may be transferable to other transition metals/transition metal oxides and their nitrides. This will diversify the toolkit of nonlinear optical materials available in the thin-film form, which in its current state is severely lacking.

[1]R. Kuis, T. Gougousi, et al, *ACS Photonics*, vol. 6, no. 11, pp. 2966–2973, Nov. 2019, doi: 10.1021/acsphotonics.9b01176.

TF-ThP-2 Water Transfer of Electronic Circuits on Flexible and Stretchable 3D Objects*, Issraa Shahine,* Nantes Université, CNRS, Institut des Matériaux de Nantes Jean Rouxel (IMN). iété d'Accélération du Transfert de Technologie, SATT Ouest ValorisatSocion SAS, France*; M. Harnois,* Université Rennes 1, CNRS, Institut d'Électronique et des Télécommunications de Rennes (IETR), France*; P. Tessier,* Nantes Université, CNRS, Institut des Matériaux de Nantes Jean Rouxel (IMN), France

There is a growing need for products that integrate active electronic devices on the surface of everyday complex objects to make them smarter and more connected. Often the presence of electronic circuits on the surface must remain relatively discreet. It is then necessary to have transparency of the circuit connections. It is a main concern of the field of 3D electronics for "smart objects" and "smart sensors" as an important part of display devices (touch screen and display), energy storage devices (solar cells and super capacitors), and wearable medical devices (electronic skin).

Herein, we use a new and original process for transferring 3D electronic circuits, to produce the interconnection of the transferred circuits over 3D objects conserving their optical, electronic and mechanical properties, to finally serve as flexible transparent conductive electrodes (FTCE).The aim is to connect SMD (surface mounted device) to the defined design circuits to validate the overall operation of the object at the level of detection, display and communication functions.

For this aim, we fabricate, by physical vapor deposition (PVD) method, flexible, stretchable and transparent nanoporous gold designs resulted by applying dealloying process to ultra-thin Au-Cu alloy thin films using acidic vapors.[1] [#_ftn1] These designs are transferred into defined flat and/or 3D surfaces according to the process of film-based patterns transferred to 3D object surfaces.[2] [#_ftn2] This new, powerful and robust technology allows a good transfer of manufactured lines with correct performances concerning the transmittance and sheet resistance of the transferred thin films to deformation.

The transfer into flexible PET surfaces allows the conservation of the electrical properties of the design upon deformation. They have good sheet resistance values ranging from few to about tens of ohms per square (Ω/□), with a transparency of the order of 50%, while maintaining exceptional stability under severe mechanical deformations (bending).

[1] [#_ftnref1]*Chauvin et al. (2019), NPJ Flexible Electronics, 3(1), 1-6.*

[2] [#_ftnref2]*Le Borgne et al. (2017), ACS applied materials & interfaces, 9(35), 29424-29429.*

TF-ThP-3 Magnetic Field Assisted Epitaxial Growth of Magnetite Films*, Adam Dziwoki,* Jerzy Haber Institute of Catalysis and Surface Chemistry PAS, Poland*; B. Blizniuk,* Jerzy Haber Institute of Catalysis and Surface Chemistry, PAS, Ukraine*; K. Freindl, J. Korecki, N. Spiridis,* Jerzy Haber Institute of Catalysis and Surface Chemistry, PAS, Poland

Modern spintronics requires materials, usually thin films and heterostructures, with controllable and programmable magnetic properties. One of the key properties is magnetic anisotropy that determines the orientation of magnetization and its response to an external magnetic field (MF). In well-defined epitaxial films the main contributions to the effective magnetic anisotropy are shape, magnetocrystalline, surface/interface and magnetoelastic/strain anisotropy terms. Molecular beam epitaxy (MBE), which is the most widely used method of growing magnetic heterostructures allows certain level of indirect control of the magnetic properties by controlling elementary growth processes through substrate temperature, deposition rate and partial pressure of reactive gases. Additionally, external agents can be used, such as plasma generation or ion beams. Other factors, including external stimuli, have been only occasionally applied in physical vapor deposition of thin films. In particular, due to the limitations of the MBE technology, examples of application of external fields (in particular MF) *in situ* during growth, as well during *in situ* post-deposition treatment are scarce. Here we present MF-assisted epitaxial growth of magnetite Fe_3O_4(001) films on MgO(001) and Fe_3O_4(111) on Mg(111).

The magnetite films were deposited in a multi-chamber ultra-high vacuum (UHV) system (base pressure $5\cdot10^{-10}$ mbar) including MBE facility, typical surface characterization tools (LEED, AES, STM) and Conversion Electron Mossbauer Spectroscopy (CEMS). We used the typical reactive deposition of metallic ^{57}Fe in O_2 (partial pressure $5\cdot10^{-6}$ mbar) [1]. The use of the ^{57}Fe isotope facilitated CEMS measurements. external MF can be applied during deposition by combination of modular sample holders transferable between two stations of a 4-axis manipulator that are specialized for a given step in the MBE process. The MgO substrates were mounted on "flag-style" (FS) sample plates and the corresponding manipulator station enables those preparation steps that do not require MF. MF can applied using PTS-style sample holders (PREVAC) incorporating permanent magnets and receiving the FS plates. The magnetic field configurations during deposition can be 100 mT in-plane and 250 mT out-of-plane for the two holder types at maximum deposition temperature of 400°C.

The role of external MF for the in-plane and out-of-plane magnetic anisotropy in the Fe_3O_4(001) and Fe_3O_4(111) film is revealed by the CEMS analysis that is able to distinguish between different magnetization orientation in the virgin magnetization state.

[1] J. Korecki et al. Thin Solid Films. 412(2002)14.

Supported by NCN 2020/39/B/ST5/01838

TF-ThP-4 Spectra Analyses of Antirreflection Coatings and Hydrogeneted Amorphous Silicon Deposited at Room Temperature for Silicon Photovoltaic Cells Aplications, *H. da Silva Alvarez, A. Roberto Silva, F. Hummel Cioldin, L. Carvalho Jayme Espindola, **José Alexandre Diniz**,* University of Campinas, Brazil

For the application in c-Si PV cells, this work has as its main objective, the analysis of antireflection coatings of thin oxides (TiO_2, Al2O3, Ta_2O_5) and nitride (SiN_x) films, deposited at room temperature, respectively by reactive sputtering or ECR-CVD, for increasing of solar cells efficiency. And of a-Si:H thin films deposited in an ECR-CVD system with RF frequencies of 1W, 3W, and 5W (a-Si:$H_{1W/3W/3W}$), for variations in their hydrogen concentration, after and before the diffusion of aluminum (Al) at the low temperature of 450 °C for future use as emitter layer. Using a UV/VIS/NIR spectrophotometer with an integrating sphere, the total reflectance of these films was calculated by comparing them with the spectra of a polished c-Si control sample (ΔR_{Total}). For the ARC films, ΔR_{Total} higher than 50% were achieved, with the largest ones coming from SiN_x, with 58.6%, and Ta_2O_5, 56.5%. Their respective minimum (R_{min}) were 1.4% and 2.5% at 610 nm and 600 nm – close to the maximum energy in the solar spectrum at 630 nm. The TiO_2 and Al_2O_3 films had corresponding ΔRTotal of 54.6% and 51.7%, with R_{min} of 5.3% and 5.9%, at 580 nm and 530 nm – shifted towards the UV region compared to the ideal value of 630 nm. For the a-Si:H films, it was observed a reduction of the polished c-Si reflection after their deposition, with the best result coming from the a-Si:H_{3W} film with 47.4 %, with R_{min} = 1.4 % at 630 nm. Followed by the sample with the a-Si:H_{5W} film with ΔR_{Total} = 35.1 % and R_{min} = 11.6 % at 670 nm. While, for the a-Si:H_{1W} film, a ΔR_{Total} = 8.2 % was obtained, with R_{min} = 3.0% at 570 nm. This low ΔR_{Total} value of the a-Si:H_{1W} sample is due to the presence of greater reflectance values on its spectra in the regions between 440 nm and 500 nm and 660 nm and 1100 nm when compared with the polished c-Si control sample. After a quickly sputtering deposition (20 s) of an ultrathin Al film and its diffusion for 30 min at 450 °C, Al-$Si_{1W/3W/5W}$ films were produced. After this process, the Al-Si_{5W} has now the best results with ΔR_{Total} = 24.8 %, R_{min} = 20.0 % at 750 nm, and the smallest change in its ΔRTotal. While the Al-Si_{3W} has an intermediate value of ΔRTotal = 8.2%. And the Al-Si_{1W} has a higher reflectance than the polished c-Si substrate with ΔRTotal = -12.6%, negative for this reason. In addition, as the spectra of the films have a similarity with the polished c-Si in the UV region, a change in their crystalline structure could be inferred, probably induced by the Al diffusion.

TF-ThP-5 Characteristics of Low Temperature Deposited SiO_2 Film based on Very High Frequency Plasma Enhanced Atomic Layer Deposition with Substrate Bias, ***Yongki Lee**, H. Kim, G. Ahn, G. Yeom,* Sungkyunkwan University (SKKU), Republic of Korea

This study investigated the effect of very high frequency (VHF) plasma and substrate biasing on the surface chemical reaction and the surface damage on SiO_2 film deposited at low substrate temperatures by Plasma-enhanced atomic layer deposition (PE-ALD) system. PE-ALD uses plasma to deliver the energy required for chemical reactions and it can be useful in lowering substrate temperature and increasing the density of material during PE-ALD, however, it can also contaminate or damage the substrate by high energy ions in the plasma. In addition, the substrate biasing may also cause unnecessary effects, especially in non-metallic materials such as preferential sputtering of high sputter yield component, charging, etc. In this study, the effect of substrate biasing was optimized while increasing the density of the plasma using VHF plasma. By applying an appropriate bias voltage to the substrate with VHF plasma, it was possible to deposit stoichiometric SiO_2 films with more rigid properties and even at a lower temperature. These results were investigated for both bare and pattern wafers. Therefore, by using optimal combinations of VHF plasma and substrate biasing, improved properties of SiO_2 films deposited at low temperatures in PE-ALD based systems could be realized. SiO_2 has good insulation performance when it is deposited at least 350°C, therefore, if this can be realized at the level of 50°C by using substrate biasing and VHF plasma, it will be helpful to the fabrication of semiconductor devices using new materials. In this presentation, the detailed properties of materials and plasmas deposited by substrate biasing and VHF plasma will be presented.

TF-ThP-6 Sio_2 Bottom-Up Trench Fill of a High Aspect Ratio Hole by Plasma Enhanced Atomic Layer Deposition Using a Very High Frequency Plasmas and Inhibitor Surface Treatment, ***Gyuhwan An**, H. Kim, Y. Lee, G. Yeom,* Sungkyunkwan University (SKKU), Republic of Korea

As the semiconductor device size is decreased to nanoscale, even though various trench fill methods such as HARP (High Aspect Ratio Process), HDP (High Density Plasma), and SOG (Spin On Glass), etc. are utilized, the SiO_2 fill process is facing limitations and has become one of the important processes as semiconductor devices become smaller and as the aspect ratio of the trench is increased significantly. In this study, the effects of capacitively coupled plasma-type very high frequency plasmas (VHF) and inhibitor surface treatment during the plasma enhanced atomic layer deposition with DIPAS (Di-isopropylamino Silane]. Formula, H3Si[N{(CH)(CH3)2}] precursor on the SiO2 trench fill characteristics were investigated to improve performance of trench fill, and especially, to obtain the bottom-up type SiO2 fill with low defects such as seam and voids. The deposition film quality was verified through wet etch rate (WER. diluted HF), X-ray photoelectron spectroscopy (XPS), and fourier transform infra-red (FT-IR) analysis, and the analysis was conducted according to the frequency of the plasma source and with different inhibitor conditions. The improvement of fill performance in patterns using inhibitor was analyzed with scanning electron microscopy while changing the trench aspect ratio from 15:1 to 40:1.

TF-ThP-8 Using Metal Precursors to Passivate Surfaces for Area Selective Deposition, ***Kinsey Canova**, L. Souqui, G. Girolami, J. Abelson,* University of Illinois at Urbana-Champaign

We previously showed that co-flowing a non-reacting, gas phase inhibitor during chemical vapor deposition (CVD) greatly enhances the area-selective deposition (ASD) of a metal film on metal instead of on oxide substrates.Here, we employ CVD precursors, which ordinarily react to grow metallic films at temperatures ≤ 300 °C, to inhibit nucleation. This occurs in a temperature window above the onset temperature (T_g) where the intended growth precursor will react to grow film, but below the onset temperature where the second precursor – here acting as an inhibitor – reacts.The latter strongly adsorbs on, and decreases the reactivity of, nucleation sites on the intended non-growth surface.The advantages of using precursors as inhibitors are that: (i) potential “inhibitor” precursors can be identified as those with dense adsorption on the non-growth surface and low reactivity towards the ligands of the intended growth precursor; (ii) they are easily integrated into the CVD process flow; and (iii) they can later be removed from the surface by thermal desorption, pyrolysis, or an atomic layer deposition half-reaction.The precursors we use as inhibitors are $Hf(BH_4)_4$ (T_g = 170 °C) or $Al(CH_3)_3$ (T_g = 300 °C), and these precursors respectively block growth from $AlH_3N(CH_3)_3$ (T_g = 130 °C) or $Hf(BH_4)_4$. Experiments with parallel dosing on metal (growth) and oxide (non-growth) surfaces are used to show the enhanced selectivity from this route. We summarize results by proposing selection criteria for other precursor-inhibitor systems: sort precursors by the T_g, select a precursor for the desired film, then choose an inhibitor that has a higher T_g than, and is unreactive towards, the desired film precursor.For ASD, the inhibitor must densely adsorb and passivate the sites that normally lead to nucleation, e.g., hydroxyl or defect sites on oxide surfaces, and there must be surfaces intended for growth where it adsorbs sparsely or not at all.

TF-ThP-9 Amorphous GeSe Thin Films Prepared by Magnetron Co-Sputtering with Rapid Thermal Annealing for UV Optoelectronic Applications, *S. Pech,* Chosun University, Cambodia*; **Sara Kim**, Y. Jun, N. Kim,* Chosun University, Republic of Korea

GeSe is one of the IV-VI semiconductors with a p-type conductivity and a modest band gap, which gives rise to potential in optoelectronic applications such as photodetectors for communication, imaging, remote sensing, and spectroscopy due to its relative earth-abundance, simple binary composition, and non-toxicity [1,2]. The GeSe was noted as a good photoresponse over a broad range of wavelengths from ultraviolet (UV) to near-infrared with on/off switching properties [3]. In this study, GeSe was deposited by using the radio frequency magnetron co-sputtering systems with Ge and Se targets. The GeSe thin films were annealed as an increase in the annealing temperature from 300 to 500 ℃ by using a rapid thermal annealing system. Compositions and surface characteristics of the GeSe thin films were examined by using an energy dispersive X-ray spectroscopy and a field-emission scanning electron microscope. The surface morphological profile and Crystal structure of the GeSe thin films were analyzed by using an atomic force microscope and X-ray diffraction. Optical properties and Hall characteristics of the GeSe thin films were analyzed by using a UV-Visible spectrometer and Hall effect measurement system. As a result of the analyses, the amorphous nature of the selected thin films was verified in all annealing temperature conditions, and a slight compositional difference occurred; however, a sudden difference in UV transmittance of the GeSe thin films occurred in specific annealing temperature conditions.

Acknowledgment: This work was supported by the Gwangju·Jeonnam Local Energy Cluster Manpower Training of the Korea Institute of Energy

Technology Evaluation and Planning (KETEP) grant funded by the Korea government Ministry of Trade, Industry and Energy (No. 20214000000560).
[1] Amir Muhammad Afzal et al., ACS Appl. Mater. Interfaces 13, 47882 (2021). [2] Ding-Jiang Xue et al., J. Am. Chem. Soc. 139, 958 (2017). [3] Zhenhua Wang et al., ACS Appl. Electron. Mater. 1, 2236 (2019).

TF-ThP-10 Considering XPS Characterisation of Ultra-Thin Films*, J. Counsell, S. Coultas,* Kratos Analytical Inc., UK*; **Christopher Moffitt**,* Kratos Analytical Inc.

Shrinking device dimensions has increased the use of atomic layer deposition (ALD) due to the need for increased control of layer thickness and uniformity. The ability to deposit high dielectric constant (high-k) films via ALD has allowed for their widespread use in a swath of optical, optoelectronic, and electronic devices.

For device design control and optimisation, it is vital to have accurate, quantitative methods to determine thicknesses and structure. We apply and discuss different thickness calculations using both conventional 1486eV and high-energy AgXPS (Ag Lα radiation - 2984eV) to elucidate the structure of ALD thin films of hafnia, alumina and a loayer combination of both.

TF-ThP-11 Characterization of Polycrystalline Hf-doped Ga_2O_3*, **Sara Chamberlin**, V. Singh,* Washington and Jefferson College*; S. King,* University of Wisconsin - La Crosse

Previous work has shown low concentrations of hafnium (Hf) incorporated into Ga_2O_3 single crystals act as a shallow donor, increasing carrier concentrations and lowering the resistivity of the crystal [1,2]. However, only a single concentration of Hf was considered within these studies. To investigate the impact that Hf concentration has on the optical, structural, and morphological properties of the material, polycrystalline films of Hf-doped Ga_2O_3 were deposited at room temperature by reactive RF-sputtering onto silicon and fused silica substrates with varying concentrations of Hf, and were subsequently characterized by spectroscopic ellipsometry, UV-VIS spectrophotometry, x-ray diffraction, x-ray photoelectron spectroscopy, and atomic force microscopy.

Initial results show that all films, regardless of Hf concentration, are initially amorphous, but crystalize as β-Ga_2O_3 upon subsequent annealing, with the possibility of phase segregation when Hf concentrations reach approximately 3 at. %, giving an indication as to the solubility limit of Hf in Ga_2O_3. Spectroscopic ellipsometry measurements show that the index of refraction of the film is altered by Hf incorporation, while UV-Vis measurements show that the optical bandgap is not significantly altered. These results suggest that Hf-doped Ga_2O_3 may find use in optoelectronic devices and applications.

[1] https://iopscience.iop.org/article/10.1088/1361-6641/ab75a6

[2] https://aip.scitation.org/doi/10.1063/5.0062739

TF-ThP-12 A Novel Direct Current Chemical Vapor Deposition (DC-CVD) Reactor for Large Area Diamond Deposition*, G. Major, A. Lizarbe,* Brigham Young University*; B. Lawrence,* Exolv*; **Matthew Linford**,* Brigham Young University

Diamond has diverse applications because of its high hardness, thermal conductivity, chemical inertness, high melting point, and high refractive index. Synthetic diamond is grown in a variety of ways, each having its advantages and disadvantages. For example, high quality, single crystal material can be grown by the high-pressure high-temperature (HPHT) method. However, the size of HPHT diamonds is limited by the size of the anvils used to produce them, and diamond thin films are not possible. Microwave chemical vapor deposition (MWCVD) is widely practiced, where MWCVD reactors are relatively inexpensive. However, MWCVD suffers from both significant plasma inhomogeneities across its growth area, as well as a limited growth area. Here, we describe a novel system based on direct current (DC) CVD, which, when compared to MWCVD, allows for larger growth areas, single-crystal growth, and more uniform growth due to a more consistent temperature and plasma across the growth surface. Our system has a growth diameter of 130 mm, which, in part, leads to a somewhat slower growth rate. However, the larger growth area allows for increased production overall. Diamonds produced in this reactor have been analyzed by Raman spectroscopy, X-ray topography, electron spin resonance, and optically detected magnetic resonance. These analyses showed minimal non-diamond growth, few defects, and uniformly oriented growth among the samples. Future developments include adding dopants, increasing diamond quality, exploring nitrogen vacancies for use in quantum computing, and other novel applications that are made accessible because of the reactor design.

TF-ThP-13 Surface Modification of Additively Manufactured Materials via Stress Gradients on Thin Film Growth*, **Andrew Miceli**, S. Stagon,* University of North Florida

Thin surface coatings, ranging from nanometers to microns thick, are commonly used to modify the performance of parts made from injection molding, machining, and 3D printing. These surface coatings, often composed of metal or metal oxide/nitride, are commonly added through physical vapor deposition (PVD). As these coatings are grown in kinetically limited conditions, large residual stresses may form during growth. In this work, we hypothesize that these intrinsic residual stresses may be used advantageously to preferentially modify the stress state experienced by the coated part via preloading effect. First, Finite Element Modeling (FEM) is used in this study to analyze the hypothesis. Using FEM, dog-bone specimens are tested in uniaxial tension using simulated coating surface pre-load stress in both tension and compression. Local stress magnitudes are determined on average by the von-Mises stress throughout the model after simulation is completed. This model is then analyzed to determine average stress of the material and which preload stress state reduces average stress through the material. It was found that in the typical tensile test load case, tensile preloading decreases overall stress of the specimen in the gauge section by up to 12%, thus lessoning chance of failure due to this lower average stress. This FEM study will be complemented by validation experiments where 3D printing will be used to rapidly fabricate polymeric (ABS) and additively manufactured metal (316SS) parts which will be subsequently coated using PVD and tested in tension. Surface characterization of the thin films will be analyzed visually using Scanning Electron Microscopy and Microhardness tests to validate and characterize the alloy composition based on stoichiometric effects. Following surface characterization, Energy Dispersive Spectroscopy will be used to analyze chemical composition of the thin film alloy created. Following uni-axial testing, fully reserved loading will be investigated to study the effects of compressive stress in PVD coatings on fatigue and results will be translated to high-value metal 3D printed parts.

TF-ThP-14 Decoding Thickness Profiles: Conformality as a Tool to Study Process Kinetics*, **Andreas Werbrouck**,* Stanford University, Belgium*; V. Cremers, J. Dendooven, C. Detavernier,* Ghent University, Belgium

While the majority of atomic layer deposition (ALD) research is directed towards developing new precursors, reaction chemistries, and applications, fundamental research on ALD conformality is interesting in its own right. Traditionally the focus in ALD conformality research has been on understanding and optimizing the precursor exposure necessary to completely cover complex 3D structures. On the contrary, this work is concerned with incompletely covered structures – more specifically holes. As the deposition proceeds, various parts of the hole receive different exposures: the top of the structure will be exposed to more precursor than the bottom. As a result, the film thickness depth profile in a hole encodes at least the same kinetic information as a traditional saturation curve but spatially resolved instead of temporally.

In order to decode the information hidden in such a thickness depth profile, two existing feature-scale simulation models were reimplemented. The reactive diffusion in the hole can be described with either a system of coupled differential equations [10.1002/cvde.201106938] or a Markov chain simulation [10.1007/s00214-014-1465-x]. Our implementation of these models was validated and subsequently used to fit experimentally obtained profiles.

The power of fitting simulated depth profiles to experimental data was demonstrated by studying plasma-enhanced ALD. With our approach, we were able to determine the partial pressure of reactive oxygen species generated in various reactor conditions (fig. 1).

A second application is in the study of reaction kinetics. As far as we know, current literature only uses first-order Langmuir adsorption to model kinetic interactions between the precursor and the substrate. Still, real-world reaction kinetics may be more complex. By allowing the model to use a general parametrized absorption function instead of a first-order model and fitting this along with the profile, useful kinetic information can be obtained. This is demonstrated with the trimethylaluminum (TMA)-water process, where the TMA step exhibits ideal first-order kinetics, but the reaction of water with the substrate is more complex. It has been suggested previously that this reaction might have a coverage-dependent activation energy [10.1021/acs.jpcc.9b11291 [10.1021/acs.jpcc.9b11291]], and our current results confirm this finding.

TF-ThP-15 Low-Temperature Synthesis of Crystalline VO_X Films via Hollow-Cathode Plasma-Assisted ALD: Impact of Vanadium Precursor, ***Adnan Mohammad**, K. Joshi, S. Ilhom, B. Wells,* University of Connecticut; *A. Kemal Okyay,* Stanford University; *B. Willis, N. BIYIKLI,* University of Connecticut

Vanadium oxide exhibits phase-change properties at different stoichiometries including the famous metal-insulator transition (MIT) for VO_2around 70 °C shifting between monoclinic to tetragonal rutile structure phase with temperature change. Such layers have the potential to be used forlow-power electrical switches. The existing VO_x ALD reports demonstrate mainly as-grown amorphous VO_x films via thermal atomic layer deposition (ALD) using TEMAV and VTIP metal precursors and water vapor or ozone as co-reactant. These amorphous films are shown to transform in various crystalline phases using post-deposition annealing process at high temperatures (typically higher than 500 °C). However, no significant report is yet found on low-temperature as-grown VO_2 films grown by thermal or plasma-ALD.

Our main goal in this study is to demonstrate as-grown crystalline VO_x films using our customized hollow-cathode plasma-ALD reactor at substrate temperatures lower than 200 °C and to further improve the crystalline quality and transform the phase structure of the deposited VO_x film into the desired VO_2 stoichiometry. We have grown crystalline VOx thin films at substrate temperatures as low as 200 °C using TEMAV as the vanadium precursor and O_2 plasma as the oxygen co-reactant. The resulting as-grown film was crystalline V_2O_5. The recipe for the plasma-ALD experiments was as the following: 0.250 s of TEMAV pulse with 10 sccm of N_2-carrier flow, 50 sccm Ar-purge for 10 sec, 50 sccm O_2 plasma for 10 s, plasma power 50-300 W, followed by another 10 s of Ar purge. To provide enough TEMAV dose into the reactor chamber, the TEMAV precursor cylinder is heated at 110 °C. The resulting films are crystalline V_2O_5 with a growth per cycle (GPC) value reaching ~2 Å and a refractive index of 2.45. The corresponding growth process has been real-time monitored with *in-situ* ellipsometry depicting the individual chemisorption and ligand exchange surface reactions.

Having accomplished our first goal, our next step is to explore VTIP as the metal precursor: will we obtain similar as-grown crystalline VOx films and if yes, which crystal structure and stoichiometry will dominate? The gain knowledge will be used to further improve and transform the crystal structure of V_2O_5 films. The resulting VO_2 films are characterized for their temperature-dependent electrical properties to validate the MIT behavior, paving the way for prototype electronic switch devices.

TF-ThP-16 Dielectric Property on the Post-Heating Treatment of PVDF Thin Film Prepared by Atmospheric Pressure Plasma Deposition, ***Eun Young Jung**,* Kyungpook National University, Republic of Korea; *C. Park,* Milligan University; *H. Tae,* Kyungpook National University, Republic of Korea

Recent developments of piezoelectric nanogenerators (PENGs) for industrial application, will be flexible and stretchable electronic devices with light weight. The piezoelectric polymers seem to be promising alternatives for flexible PENGs. In present, polyvinylidene fluoride (PVDF) has been widely used due to its unique properties such as mechanical flexibility, high chemical resistance, biocompatibility, and high temperature resistance [1,2]. However, this PVDF polymer has still lower piezoelectric characteristics when compared with piezoelectric ceramics. Thus, it is necessary to improve the piezoelectric and dielectric property of the conventional PVDF material for flexible PENGs. Many researches have been mostly investigated on the piezoelectric polymer-nanocomposites with nano-particles in order to develop dielectric materials with high dielectric coefficient for flexible PENGs [1,3]. Accordingly, we examine the effects of the post-heating on the structural and dielectric properties of PVDF thin film deposited by atmospheric pressure plasma (APP) system. The structural and dielectric properties of PVDF thin film were systematically investigated by using field emission-scanning electron spectroscopy (FE-SEM), X-ray diffraction (XRD), Fourier transforms-infrared spectroscopy (FT-IR), LCR meter according to post-heating in order to remove the N,N-dimethylformamide (DMF) element and enhancing the chemical structure of PVDF thin film. After post-heating treatment, the amount of bubble was reduced. This result implies that the DMF solution is almost removed from PVDF thin film, and the PVDF nanoparticles are clearly observed on the surface of PVDF thin film. In FT-IR, the peak intensity at 1669 cm^{-1} for -C=O by DMF solution largely decreases after post-heating, and the post-heated PVDF thin film shows mainly two crystalline phases (α and β phases), which represents the peaks at 975 and 1402 cm^{-1} for α-phase and the peak at 1072 cm^{-1} for β-phase, respectively. The formation of two phases (α and β phases) attributed to the increment in the dielectric constant of the post-heated PVDF thin film. The capacitance and dielectric coefficient values were measured to be 96 nF and 15 at 1 kHz frequency in post-heated PVDF thin film, respectively. The detailed characteristics of the post-heated PVDF thin film using FE-SEM, FT-IR, XRD, and LCR meter are under study and will be discussed in detail.

TF-ThP-17 The Microstructure, Roughness, and Electrical Properties of v-Doped SiC Films, ***Chao-Te Lee Lee**, W. Chen, H. Chen,* Taiwan Instrument Research Institute, National Applied Research Laboratories, Taiwan

Silicon carbide (SiC) thin film with various V contents were deposited on Si(100) substrate at room temperature by RF magnetron sputtering system using sintered SiC (99.95% purity) and V (99.995 purity) targets. The as-deposited films were annealed in the temperature of 1000 ^oC under vacuum in 1 hour. Effects of V-doped and annealing on the composition, microstructure, roughness, and electrical properties of films were examined by field emission scanning electron microscopy with an energy dispersive X-ray spectroscope(SEM-EDX), X-ray diffraction (XRD), atomic force microscopy (AFM), and resistance meter. The XRD and AFM results show that all of the as-deposited films were amorphous with smooth surface. The roughness of the as-deposited films were all below 0.3 nm. After 1000 ^oC annealing, only the β-SiC(220) phase was been observed of SiC and $(SiC)_{98.2}V_{2.8}$ films. The β-SiC(100) and β-SiC(220) two phases were been observed of the others annealed films. The roughness of the annealed films were hugely increased with increasing V content when the V content is over 2.8 at.%. The roughness of the annealed$(SiC)_{63.6}V_{36.4}$ film was 9.6 nm. The electrical properties of the annealed films was similar with XRD and AFM analysis. It was demonstrated that the annealed $(SiC)_{1-x}V_x$ film was semi-insulating when the V content was over 28.2 at.%.

TF-ThP-19 Fluorine-Doped SiO_2 Films Applied to Optical Coating Deposited by Reactive Magnetron Sputtering, *B. Liao,* Taiwan Instrument Research Institute, Taiwan; ***Chien-Nan Hsiao**,* National Applied Research Laboratories, Taiwan

Porous SiO_2:Ffilms were deposited by reactive magnetron sputtering with a Si metal target at room temperature. Various ratios of O_2 to CF_4 gas were introduced to deposit SiO_2:F films. The optical properties, microstructure, surface roughness, and crystalline structure, of SiO_2:F films have been studied. The refractive index at 550 nm decreased from 1.46 to 1.39 with increasing CF_4 ratio. Then high reflection coating at 1064nm were deposited with Nb_2O_5 and SiO_2:F as high and low refractive materials.

TF-ThP-20 Low-Density SiOC Thin Films Grown by Low Temperature Plasma-Enhanced Chemical Vapor Deposition for High Performance Acoustic Bragg Mirrors, ***Julian Pilz**, N. Andrianov,* Microsystems Division, Silicon Austria Labs, Austria; *T. Sinani,* Sensor Systems Division, Silicon Austria Labs, Austria; *S. Azeem, T. Dao, M. Moridi,* Microsystems Division, Silicon Austria Labs, Austria; *G. Bruckner,* Sensor Systems Division, Silicon Austria Labs, Austria

Solidly mounted resonators are an important type of bulk acoustic wave resonators, which are applied in devices such as radio-frequency filters. To decrease acoustic losses into the substrate, dielectric Bragg mirrors are applied between the bottom electrode and the substrate within the layer stack. These mirrors typically consist of alternating high (W) and low acoustic impedance (SiO_2) films. To increase the acoustic impedance contrast and thus the performance of the mirror and resonator, one approach is to lower the acoustic impedance of the low acoustic material which depends on the density and elastic modulus. In literature, doping of SiO_2 with C has been shown to be an effective approach to reduce the dielectric function with respect to pure SiO_2.[1]

In this study, plasma-enhanced chemical vapor deposition (PECVD) is investigated for growing low acoustic impedance SiOC (carbon doped silicon oxide) thin films on 100 mm diameter Si wafers with native oxide. SiH_4, CH_4, and N_2O are used as the precursors for Si, C, and O, respectively, and Ar is added as neutral species to the processing plasma. The substrate temperature is varied from 50 °C to 350 °C, the total flow rate at a constant pressure (1.2 Torr) from 174 sccm to 698 sccm, and the CH_4/N_2O flow rate ratio from 0 to 0.2.

Generally, increasing the total flow rate and decreasing the substrate temperature leads to a decrease of the refractive index, which is used as a measure of the density of the film. At 50 °C and a total flow rate of 698 sccm, the refractive index (at 633 nm; spectroscopic ellipsometry) and the mass density (graviometry) can be tuned from 1.37 to 1.42 and 1.6 to 1.9 g/cm^3, respectively, by tuning the CH_4/N_2O ratio, with the lowest values found at CH_4/N_2O=0.08. The RMS roughness (atomic force microscopy)

increases (10-20 nm for around 500 nm thickness) and the films become softer with increasing CH_4/N_2O ratio (0-0.2), where the elastic modulus drops by 50 % (nanoindentation). Fourier transform infrared spectroscopy furthermore shows changes in the chemical structure with changing ratio of Si, C, and O bonds.

In conclusion, the study shows the potential of using a low temperature PECVD process for tuning the acoustic impedance of SiOC thin films. As the main knob the CH_4/N_2O flow ratio is investigated which allows to change the chemical and structural properties of the material, supposedly creating a more open structure and weaking the bond strength. In further studies, the films will be tested in a resonator test device and benchmarked against industrial state-of-the-art layer stacks.

[1]Grill, J. Appl. Phys., **93** (3), 1785, 2003

Thin Films Division
Room 316 - Session TF1+PS-FrM
Plasma, PVD and HIPIMS Processes for Emerging and Advanced Materials

Moderators: Joe Becker, Kurt J. Lesker Company, **Christophe Vallee**, SUNY College of Nanoscale Science and Engineering

8:40am **TF1+PS-FrM-2 Growth of c-axis Textured AlN PVD Film on a 2D-MoS_2 Seed Layer***, **Julien Patouillard,*** STMicroelectronics, France*; E. Blanquet, A. Mantoux,* SIMaP, CNRS, University Grenoble Alpes, France*; F. Gianesello,* STMicroelectronics, France*; M. Bernard, S. Cadot, R. Gassilloud, C. Raynaud,* Commissariat à L'énergie Atomique, France

Aluminum nitride (AlN) is a piezoelectric and wide bang gap material which crystallizes in a hexagonal wurtzite structure. This material arouses a certain interest in various fields of microelectronics, in particular radiofrequency (RF) devices [1–3]. Its deposition process is well-known and appears to be reproducible, using either epi-like chemical deposition solutions, or N_2-based physical deposition with Al-target. In particular, AlN deposited by Physical Vapor Deposition (PVD) exhibits a relatively large electromechanical coupling coefficient $k_t^2 \approx 6{,}5\%$. [2]

Due to the lack of bulk AlN substrates and the large lattice mismatch between AlN and silicon, AlN is usually epitaxially grown on sapphire or silicon carbide (SiC) substrates at high growth temperature (≈1000 °C) to achieve higher crystalline quality and hence better device performance [4,5]. However, high cost, limited wafer size or differences in thermal expansion coefficient between AlN and these substrates drastically limit the integration and applications of AlN.

In recent years, the emergence of 2-Dimensional (2D) materials and particularly 2D-Transition Metal Dichalcogenides (2D-TMDs) seems to be a promising approach for the growth of III-nitride. Among 2D-TMDs, MoS_2 is one of the most widely studied materials due to its availability [6,7]. MoS_2 has a natural two-dimensional structure with the sandwich-like S-Mo-S layers serving as building blocks, in which the atoms in the layer are bonded with strong covalent bonding, while the layers are packed together with weak interlayer forces [8,9]. It also presents a hexagonal structure with a close lattice matching with III-nitride (1 % to 3 %) and a chemical compatibility enabling the direct growth of these materials [4,5].

In this presentation, we will demonstrate the direct growth of c-axis textured AlN films deposited by PVD on a well-controlled and uniform MoS_2thin film elaborated by Atomic Layer Deposition (ALD). We will show how 2D materials can be advantageously implemented to improve the texturation of AlN on silicon substrate. Hence, in figure 1, the crystal quality of AlN is assessed by X-Ray Diffraction (XRD) measurements using the Rocking Curve (RC) technique. The FWMH of the omega peak at 18° (Theta 36,04° of (002)) gives a direct information on the mosaicity of the AlN layer. AlN Growth on 2D-MoS_2 seed induces a strong reduction of FWMH compared to Si-based substrate, indicating the preferential reorientation of the AlN matrix along the (002) axis, perpendicular to the substrate surface. This orientation is expected to boost the piezoelectric coefficient, which opens new field of applications on Si substrate.

9:00am **TF1+PS-FrM-3 Synthesis and Hardness of Thin-Film High-Entropy Transition Metal Ceramics***, **Nathaniel McIlwaine,*** The Pennsylvania State University*; M. Hossain,* Pacific Northwest National Lab*; J. Maria,* The Pennsylvania State University

High entropy carbides (HECs) are single phase, multicomponent materials that possess a high degree of configurational entropy on cation lattice sites and can possess enhanced thermal and mechanical properties compared to binary transition metal carbides. Group IIIB, IVB, VB, and VIB transition metal HECs with high hardness and high melting temperatures are prospective materials for refractory applications such as advanced armor, cutting tools, and spacecraft thermal protection systems.

HECs are chemically disordered crystals containing components inclined to form ternary solid solution compounds and carbon deficient phases. Multicomponent carbides produced by conventional reactive sputtering techniques, such as radio frequency (RF) and direct current (DC), are hindered in overall film quality due to uncontrolled microstructure and stoichiometry. This work is focused on the synthesis of HECs through reactive bipolar high-power impulse magnetron sputtering (HiPIMS) to overcome these conventional challenges. Through HiPIMS, HEC crystals structurally and compositionally transform as a function of the carbon to metal ratio (C/M), providing access to metallic, ceramic, and composite carbides. By increasing the methane flow rate during sputtering, this introduces a carbon-deficient metallic (C/M < 1), transitions to a stoichiometric ceramic zone (C/M ∼ 1), and finally culminate in an excess-carbon, nanocomposite regime (C/M > 1) at high methane flow rates. Combinations of X-ray diffraction, Raman spectroscopy, scanning electron microscopy, X-ray photoelectron spectroscopy, and nanoindentation/microindentation hardness measurements form these three zones. Achieving the stoichiometric ceramic zone is of particular interest to maximize the hardness of a given HEC composition. HiPIMS is able to produce HECs with ceramic zones over a larger range of methane flow rates than RF or DC sputtering.

9:20am **TF1+PS-FrM-4 Structural Evolution and Thermoelectric Properties of Flexible Mg_2Sn Films Prepared by Magnetron Co-sputtering***, **Sara Kim,** S. Kang, N. Kim,* Chosun University, Republic of Korea

Thermoelectric (TE) materials are capable of harvesting waste heat and converting it into useful electrical power which contributes significantly to improved energy efficiency. Recently, the development of flexible TE materials and devices has become a significant focus in the thermoelectric field due to the need for wearable and autonomous devices. The flexible TE materials can effectively harvest waste-heat from hot surfaces in a wide temperature range for applying to power generation in industry and human life. The anti-fluorite Mg_2X (X = Si, Ge, Sn)compounds have attracted great attention owing totheir non-toxicity, low manufacturing cost, light weight, and flexibility [1]. In this study, several un-doped Mg-Sn films were deposited onto polyimide substrates by radio frequency magnetron co-sputtering with Mg and Sn targets. Mg sputtering power was fixed while Sn sputtering power was varied to prepare Mg-Sn films with different stoichiometry. Then, Mg and Sn sputtering time was varied to prepare films with different thicknesses while the sputtering power was fixed. The TE performances as well as the flexibilityof the samples were analyzed in terms of point defects and structural evolution of the samples during flexibility test. Folding tests with different folding cycles were carried out for flexibility evaluation of the samples. The structural properties, chemical composition, and Hall characteristics of the Mg-Sn thin films before and after the folding test were analyzed using X-ray diffraction, energy dispersive X-ray spectroscopy, and Hall effect measurement system, respectively. The electrical resistivity and Seebeck coefficient as a function of temperature were simultaneously measured up to 703 K. Acknowledgement: This work was supported by the Gwangju·Jeonnam Local Energy Cluster Manpower Training of the Korea Institute of Energy Technology Evaluation and Planning (KETEP) grant funded by the Korea government Ministry of Trade, Industry and Energy (No. 20214000000560). [1] J. I. Tani, and H. Ishikawa, Thin Solid Films 692, 137601 (2019).

Thin Films Division
Room 316 - Session TF2+EM-FrM
Wide and Ultra-Wide Bandgap Thin Films: Advances in Deposition and Novel Materials

Moderators: Christophe Vallee, SUNY College of Nanoscale Science and Engineering, **Virginia Wheeler**, U.S. Naval Research Laboratory

10:00am **TF2+EM-FrM-6 AlGaN, An Enabling Ultra-Wide Bandgap Semiconductor***, **Dolar Khachariya,*** Adroit Materials*; M. Breckenridge, D. Szymanski, S. Stein,* North Carolina State University*; W. Mecouch,* Adroit Materials*; Y. Guan, P. Bagheri, S. Rathkanthiwar,* North Carolina State University*; P. Reddy, R. Kirste, S. Mita, B. Moody, J. Tweedie,* Adroit Materials*; K. Sierakowski, M. Boćkowski,* Institute of High-Pressure Physics, Poland*; E. Kohn, S. Pavlidis, R. Collazo, Z. Sitar,* North Carolina State University **INVITED**

III-nitride ultra-wide bandgap semiconductors offer a future alternative to maintain the growing demand for high-power devices. Current III-nitride devices already offer higher breakdown voltages (BV) and reduced on-resistances (R_{ON}) compared to Si and SiC. However, several power devices, such as junction barrier Schottky (JBS) diodes and superjunctions (SJ), which provide an improved BV and R_{ON} tradeoff, have not been demonstrated in III-nitrides. The major limitation is the difficulty of

achieving selective area doping. In the JBS diode, p-regions must be laterally interspersed between n-regions below the anode contact. A SJ device requires alternating lateral n- and p-type doping regions with zero net charges. Two approaches can be considered to address this challenge: ion implantation and polarity control.

Currently, III-nitrides do not possess a robust ion implantation toolbox that allows for reliable implantation control and activation. Recent advances in ion implantation for the realization of n-type AlN and p-type GaN will be discussed. For n-type AlN, Si implantation was realized with the implementation of defect quasi-Fermi level control. The highest *n*-type conductivity in AlN will be demonstrated. For p-type GaN, we demonstrate the ability to successfully achieve *p*-type conductivity via Mg implantation and post-implantation annealing at ultra-high pressure. Using this technique, GaN JBS diode with low R_{ON} and high BV will be discussed.

The inherent polar doping selectivity of GaN can be used to achieve the doping scheme for a lateral GaN p/n junction. Oxygen, which unintentionally incorporates into N-polar GaN, acts as the n-type dopant, whereas Ga-polar GaN does not readily incorporate oxygen and remains undoped. Accordingly, lateral polarity junctions (LPJs) with alternating domains of O-doped N-polar and Mg-doped Ga-polar GaN have been fabricated to realize lateral p/n junctions. For drift regions, the n-type doping in the N-polar domain (and p-type doping in the Ga-polar domain) was reduced to ~10^{17} cm^{-3}. Implementing the chemical potential control (CPC) framework and supersaturation modulated growth (SMG), a GaN LPJ with a smooth surface and equal domain heights with the necessary doping profile will be discussed.

10:40am **TF2+EM-FrM-8 CVD of Crystalline and Amorphous sp^2-BN Thin Films on Different Orientations of Al_2O_3**, *S. Sharma,* Linköping Univ., IFM, Thin Film Physics Div., Sweden*; **Laurent Souqui,*** University of Illinois at Urbana-Champaign*; H. Pedersen,* Linköping University, IFM, Sweden*; H. Högberg,* Linköping Univ., IFM, Thin Film Physics Div., Sweden

Thin films of epitaxially grown sp^2-hybridized boron nitride (sp^2-BN) in its hexagonal (h-BN) and rhombohedral (r-BN) phases have potential applications in optoelectronics and graphene technologies. Additionally, amorphous sp^2-BN (a-BN) is a promising material for electronic applications as a dielectric along with being a barrier for metal diffusion. Thin film growth of sp^2-BN is typically done using chemical vapor deposition (CVD). Growth of epitaxial sp^2-BN thin films requires high growth temperatures, above 1200 °C; for this reason, (0001) oriented sapphire (Al_2O_3) substrates are commonly used. Our study[1] investigates the growth of sp^2-BN using thermal CVD, comparing the differences in growth on Al_2O_3(11-20), Al_2O_3(1-102), Al_2O_3(10-10) and Al_2O_3 (0001), known as *a*-cut, *r*-cut, *m*-cut and *c*-cut substrates respectively, with an AlN buffer layer. For growth of sp^2-BN on these cuts, we use two boron precursors triethylborane (TEB) and trimethylborane (TMB), both along with NH_3 to investigate different chemical pathways.

Regardless of the boron precursor used, sp^2-BN growth on all the substrates was confirmed using Fourier transform infrared spectroscopy. X-ray Diffraction (XRD) 2θ/ω scans revealed that the sp^2-BN films grown on *c*-cut and *a*-cut were crystalline with the basal planes parallel to the substrate surface, while sp^2-BN films deposited on *r*-cut and *m*-cut were X-ray amorphous. XRD ϕ-scans showed the epitaxial growth of r-BN on *c*-cut and *a*-cut substrates. The in-plane relationship on the *a*-cut is r-BN[11-20]ǁ w-AlN[11-20]ǁ α-Al_2O_3[0001], which is similar to the *c*-cut. Using XRD ω-scan on the r-BN0003 peak, we determined that the crystal quality of r-BN is higher on the *a*-cut compared to the *c*-cut substrate; full width half maximum of 0.98° and 1.15° respectively. Scanning electron microscopy showed triangular shaped grains surrounded by less ordered material on the surface for the *c*-cut and *a*-cut while no such triangular features were seen on the *r*-cut and *m*-cut substrates. Our results show that epitaxial r-BN films are grown with determined in-plane orientations and with higher crystal quality on the *a*-cut. Conversely, a-BN films can be grown using the *r*-cut and *m*-cut substrates.

To advance the field, we will apply advanced analytical microscopy to study the differences locally, in terms of crystallinity, chemical bonding, and the influence of carbon in our deposited films. Additionally, other aspects of amorphous growth will be investigated.

(1) Sharma, S et al. Chemical Vapor Deposition of Sp^2 -Boron Nitride Films on Al_2O_3 (0001),(11-20),(1-102),and(10-10) substrates . *J. Vac. Sci. Technol. A***2022**,*40*(3),033404

11:00am **TF2+EM-FrM-9 Investigating SiC/Graphene/SiC(0001) Remote Epitaxy Using Hot-wall CVD**, ***Daniel J. Pennachio,*** US Naval Research Laboratory*; J. Hajzus,* ASEE Postdoctoral Fellow at US Naval Research Laboratory*; A. Lang,* US Naval Research Laboratory*; R. Stroud,* Former employee of US Naval Research Laboratory*; R. Myers-Ward,* US Naval Research Laboratory

Remote epitaxy (RE) is a promising new technique for epitaxial film removal and substrate reuse that utilizes monolayer graphene as a release layer [1]. Graphene grown directly on SiC(0001) substrates through Si sublimation or through propane chemical vapor deposition (CVD) is an ideal platform for remote epitaxy of wide bandgap (WBG) semiconductors as there is no need for a graphene transfer step, reducing the risk of introducing contamination or defects that can complicate the study of the remote epitaxy process. In addition, this materials system is compatible with commercially-viable WBG semiconductor growth and processing. However, SiC CVD growth is typically conducted using high-temperature hydrogen-based chemistries that could damage or remove graphene. This study investigates the effect of alternate CVD growth conditions on SiC/graphene/SiC(0001) remote epitaxy and optimizes CVD parameters to produce high-quality SiC epilayers while reducing damage to the graphene barrier. In addition, since the effect of epitaxial graphene features such as SiC macrostep morphology and associated layer inhomogeneity on the RE process is currently unknown, graphene preparation and associated morphology is varied to explore its effect on SiC epilayer formation.

Semi-insulating nominally on-axis 6H-SiC(0001) and n-type 4° off-axis 4H-SiC(0001) substrates were used to produce different SiC surface morphologies and graphene layer numbers. Ar:H_2 process gas flow ratio, growth precursor C/Si ratio, and growth temperature were optimized during hot-wall CVD RE to promote smooth film morphology. Nomarski optical microscopy, scanning electron microscopy, and atomic force microscopy found CVD deposition at 1620°C with Ar/H_2 ratios <20/5 slm, and C/Si ratios <1.55 to have the smoothest surface morphology and fewest polytype inclusions. Substrates with offcuts <0.1° from SiC(0001) exhibited lower epilayer macrostep density, but showed evidence of polytype impurities and 3D growth at C/Si ratios > 1.0. Point defect density in RE SiC epilayers using a graphene interface was shown to be lower than SiC homoepitaxy using similar conditions without graphene. Cross-sectional transmission electron microscopy was utilized to assess the growth interface and graphene layer integrity after CVD growth. Through this study, optimal RE growth processes are suggested for a balance of graphene survivability and SiC film morphology.

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

11:20am **TF2+EM-FrM-10 Sputter Deposition of III-N Thin Films**, ***Joshua Nordlander,*** The Pennsylvania State University*; Z. Sitar,* North Carolina State University*; J. Maria,* The Pennsylvania State University

In this presentation, we demonstrate that reactive High-Power Impulse Magnetron Sputtering (HiPIMS) is an effective alternative for depositing high quality, epitaxial III-N thin films. In contrast to conventional direct current (DC) sputtering, HiPIMS provides the needed kinetic energy and ionization fraction to establish a sufficiently reactive environment to promote full nitridation.Specifically, the low duty cycle regime of HiPIMS provides access to kW/cm^2 peak power densities without target degradation and thus dramatically increased metal reactivity. In addition, adding an opposite polarity voltage pulse between the target bombarding events, known as a kick pulse, further allows one to tailor both the adatom landing energy on the substrate surface, and mitigate target poisoning.

This unique capability set enables us to prepare high crystal quality epitaxial InN thin films with low out-of-plane mosaicity and electron mobilities in excess of 400 cm^2/Vs with a step-and-terrace microstructure when deposited on AlN-nucleated sapphire substrates.Equilibrium supersaturation models are useful for predicting the surface microstructure of these films by varying the V/III ratio or deposition temperature.

In addition, homoepitaxial GaN thin films can be deposited at temperatures below 600°C with smooth surface morphologies characterized by c/2 steps and terraces.The presentation will focus on the relationships between sputtering parameters and III-N thin film crystal quality, surface morphology, and growth rate.

11:40am **TF2+EM-FrM-11 Thickness Dependent Properties of Ferroelectric Boron-Substituted Aluminum Nitride Thin Films***, **John Hayden,** J. Nordlander, W. Zhu, S. Trolier-McKinstry, J. Maria,* Pennsylvania State University

Recently discovered wurtzite structured ferroelectrics are interesting as next generation materials for ferroelectric memory devices, however they suffer from large leakage currents at small film thicknesses. In this work, we investigate the thickness dependent properties of ferroelectric boron-substituted aluminum nitride based thin films deposited by magnetron co-sputtering. Films grown on tungsten coated sapphire substrates show robust ferroelectricity for thicknesses as small as ~100 nm. Polarization hysteresis measurements of films thinner than 100 nm show inflated remanent polarization values from leakage currents. Electron microscopy studies and thickness dependent x-ray rocking curve measurements indicate there is a defect rich region near the film-electrode interface with reduced film crystallinity and out-of-plane mosaicity. In an attempt to improve film quality near the interface, films are grown on a variety of electrode materials with varying chemical and structural similarities to wurtzite structured aluminum nitride. Tungsten nitride is chosen as it is nitrogen containing, yet structurally dissimilar to aluminum nitride, while indium nitride is chosen because it is isostructural to aluminum nitride. For films grown on tungsten nitride, roughness and leakage currents decreased with decreasing electrode thickness, though no substantial improvements compared to films grown on W were observed. Films grown on epitaxial indium nitride/aluminum nitride/sapphire stacks adopt the stepped surface morphology of the InN and exhibit significantly narrower rocking curve widths compared with films grown on W. Film crystallinity, leakage current, and ferroelectric properties are investigated as a function of indium nitride surface morphology and ferroelectric film thickness.

Author Index

Bold page numbers indicate presenter

— A —
Abelson, J.: TF2+AP+SE+SS-WeM-5, 27; TF-ThP-8, 45; TF-TuM-5, 12
Abu Qahouq , J.: TF2-WeA-10, 33
Agarwal, S.: TF+AS-ThA-6, 43
Ahn, G.: TF-ThP-5, 45
Ahsan, R.: TF+EM-MoA-1, 7
Ahuja, K.: TF+EM-MoM-9, 5
Alexandre Diniz, J.: TF-ThP-4, **45**
Alexeev, A.: BI1+AS+EM+NS+SE+TF-TuM-1, 10
Allegret-Maret, S.: PS2+TF-WeM-13, 25
Almalki, S.: TF+EM-MoM-1, 5
Alupothe Gedara, B.: SS+AS+TF-MoM-10, **4**
An, G.: TF-ThP-6, **45**
Anasori, B.: TF2+2D-TuA-4, 20
Anayee, M.: AS+2D+EM+MS+NS+SS+TF-ThA-3, 41
Anderson, K.: TF2+AP+SE+SS-WeM-6, 28
Andrew, T.: TF+EM-MoA-5, 8; TF+EM-MoA-6, 8; TF1+SE-WeM-2, **25**
Andrianov, N.: TF-ThP-20, 47
Armini, S.: PS1+AP+TF-WeM-3, **21**
Artyushkova, K.: AS+2D+EM+MS+NS+SS+TF-ThA-3, **41**
Arunachalam, A.: TF+AS-ThA-5, 43
Asenath-Smith, E.: SE+AS+BI+SS+TF-ThM-5, 37
Attia, S.: SS+AS+TF-MoM-3, 3
Azeem, S.: TF-ThP-20, 47
Azina, C.: SE+MN+PS+TF-WeA-3, 30
Aziz, D.: TF3+MS-WeM-13, 28
— B —
Bagheri, P.: TF2+EM-FrM-6, 49
Bahr, A.: SE+MN+PS+TF-WeA-10, 30
Bajcsy, P.: LS2+2D+AS+TF-TuA-9, 17
Bale, R.: AP+2D+AS+EM+PS+SS+TF-MoM-9, 2
Balogun, S.: TF1+SE-WeM-6, **26**
Baloukas, B.: SE+AS+BI+SS+TF-ThM-1, **36**
Banerjee, P.: AP+AS+EM+HI+PS+SS+TF-TuM-6, 10; TF+AS-ThA-5, 43
Banerjee, S.: EM+MN+TF-ThM-4, 34
Baraket, M.: TF2-WeA-7, 32
Barlaz, E.: PS1+AP+TF-WeM-10, 22
Barnes, B.: MS+AP+AS+TF-MoA-1, **7**
Barton, K.: TF+EM-MoA-4, 8; TF1+AP-WeA-2, 31
Basu, K.: TF+AS-ThA-5, 43
Beilliard, Y.: PS1+TF-TuA-12, 19
Bent, S.: AP+2D+AS+EM+PS+SS+TF-MoM-8, 2; TF1+SE-WeM-11, 26; TF2+AP+SE+SS-WeM-1, 27
Bernard, M.: TF1+PS-FrM-2, 49
Berquist, Z.: TF-TuM-10, 13
Berriel, S.: TF+AS-ThA-5, **43**
Bhattacharya, S.: EM+MN+TF-ThM-6, **35**
Bielefeld, J.: AP+2D+AS+EM+PS+SS+TF-MoM-9, 2
Bielinski, A.: TF-TuM-10, 13
Binder, A.: EM+MN+TF-ThM-5, 34
Birch, M.: LS2+2D+AS+TF-TuA-10, 17
Biyikli, N.: PS1+AP+TF-WeM-11, 22
BIYIKLI, N.: TF-ThP-15, 47
Blanc, R.: PS1+TF-TuA-4, **18**
Blanquet, E.: TF1+PS-FrM-2, 49
Blatnik, M.: TF1+SE+SS-ThM-4, 40
Bliem, R.: SE+AS+BI+SS+TF-ThM-13, 38
Blizniuk, B.: TF-ThP-3, 44
Blumenschein, N.: MI+2D+TF-ThM-12, 36
Boćkowski, M.: TF2+EM-FrM-6, 49
Bogdanovski, D.: AS+2D+EM+MS+NS+SS+TF-ThA-5, 41; SE+MN+PS+TF-WeA-3, 30
Boixaderas, C.: PS1+TF-TuA-1, 17
Bonvalot, M.: AP+2D+AS+EM+PS+SS+TF-MoM-1, 1; AP+AS+EM+HI+PS+SS+TF-TuM-3, 9; TF+AP-ThM-12, **39**
Boreman, G.: TF+EM-MoA-3, 7
Borges, J.: PS1+TF-TuA-12, **19**
Boris, D.: PS1+AP+TF-WeM-1, **21**; PS1+AP+TF-WeM-5, 21; TF+AS-ThA-3, 42
Boscher, N.: TF2-WeA-9, 33
Boulard, F.: PS1+TF-TuA-11, **19**
Boutaud, B.: PS2+TF-WeM-10, 24
Boyd, J.: EM+MN+TF-ThM-6, 35
Bozdog, C.: MS+AP+AS+TF-MoA-8, **7**
Breckenridge, M.: TF2+EM-FrM-6, 49
Bright, V.: AP+PS+TF-TuA-12, 16
Brock, C.: TF3+MS-WeM-12, **28**
Bruce, R.: PS1+TF-TuA-3, 18; PS2+TF-WeM-12, 24
Bruckner, G.: TF-ThP-20, 47
Bruehl, J.: PS1+AP+TF-WeM-10, 22
Brummer, A.: TF3+MS-WeM-13, 28
Brunet, L.: PS1+TF-TuA-11, 19
Burger, J.: TF1+AP-WeA-4, 32
Burghard, M.: LS2+2D+AS+TF-TuA-10, 17
Burtscher, M.: SE+AS+BI+SS+TF-ThM-4, 37
Butera, R.: TF1+SE+SS-ThM-3, 39
Butkus, B.: AP+AS+EM+HI+PS+SS+TF-TuM-6, **10**
Buzi, L.: PS1+TF-TuA-3, **18**
— C —
Cabral, M.: EM+MN+TF-ThM-3, 34
Cadot, S.: TF1+PS-FrM-2, 49
Campbell, P.: MI+2D+TF-ThM-12, 36
Canova, K.: TF2+AP+SE+SS-WeM-5, **27**; TF-ThP-8, **45**
Canvel, Y.: PS1+TF-TuA-9, **18**
Caroff, C.: TF2+AP+SE+SS-WeM-5, 27; TF-TuM-5, 12
Carvalho Jayme Espindola, L.: TF-ThP-4, 45
Castagna Ferrari, V.: TF-TuM-3, **12**
César, R.: TF+EM-MoM-3, 5
Chae, H.: TF+EM-MoA-1, 7
Chamberlin, S.: TF-ThP-11, **46**
Chandrasekaran, A.: TF3+MS-WeM-12, 28
Charyton, M.: TF2-WeA-9, **33**
Chen, C.: PS2+TF-WeM-12, 24
Chen, H.: TF-ThP-17, 47
Chen, W.: TF-ThP-17, 47
Chen, Y.: TF-TuM-10, 13
Cheng, H.: PS1+TF-TuA-3, 18
Cheng, R.: TF2+2D-TuA-4, 20
Chevolleau, T.: AP+2D+AS+EM+PS+SS+TF-MoM-1, 1
Cho, T.: TF+EM-MoA-4, **8**; TF1+AP-WeA-2, 31
Choi, T.: PS1+AP+TF-WeM-10, 22
Chowdhary, N.: TF-ThP-1, **44**
Chrit, F.: BI1+AS+EM+NS+SE+TF-TuM-1, 10
Chu, J.: BI1+AS+EM+NS+SE+TF-TuM-2, **11**
Clark, R.: AP+2D+AS+EM+PS+SS+TF-MoM-4, 1
Coclite, A.: TF1+SE+SS-ThM-4, 40
Coffey, B.: AP+AS+EM+HI+PS+SS+TF-TuM-12, 10; AP+AS+EM+HI+PS+SS+TF-TuM-4, 9
Cohen, G.: PS2+TF-WeM-12, 24
Coll, M.: TF1+SE+SS-ThM-1, **39**
Collazo, R.: TF2+EM-FrM-6, 49
Conley, J.: TF+EM-MoM-4, 5
Consiglio, S.: AP+2D+AS+EM+PS+SS+TF-MoM-4, 1
Cooper, J.: EM+MN+TF-ThM-5, 34
Cotrin, R.: TF+EM-MoM-3, 5
Couet, S.: PS1+TF-TuA-4, 18
Coultas, S.: TF-ThP-10, 46
Counsell, J.: TF-ThP-10, 46
Crawford, G.: SE+AS+BI+SS+TF-ThM-5, 37
Creatore, M.: TF+AP-ThM-13, 39; TF1+SE-WeM-13, 26
Cremers, V.: TF-ThP-14, 46
Crittenden, S.: MI+2D+TF-ThM-1, 35
Cunge, G.: PS2+TF-WeM-13, 25
Czettl, C.: SE+AS+BI+SS+TF-ThM-4, 37; SE+MN+PS+TF-WeA-11, 31; SE+MN+PS+TF-WeA-7, 30
— D —
da Silva Alvarez, H.: TF-ThP-4, 45
Dabas, S.: AP+AS+EM+HI+PS+SS+TF-TuM-6, 10
Dahlqvist, M.: SE+AS+BI+SS+TF-ThM-10, **38**
Dameron, A.: TF1+AP-WeA-4, 32
Dao, T.: TF-ThP-20, 47
Darnon, M.: PS1+TF-TuA-12, 19
Dasgupta, N.: TF+EM-MoA-4, 8; TF1+AP-WeA-2, 31; TF-TuM-1, **12**; TF-TuM-10, 13
D'Attilio, N.: SE+AS+BI+SS+TF-ThM-5, **37**
Daugherty, M.: LS2+2D+AS+TF-TuA-9, 17
Davis, R.: EM+MN+TF-ThM-3, 34
Davoodabadi, A.: TF-TuM-10, 13
Day, P.: TF-TuM-12, 13
de Visser, A.: SE+AS+BI+SS+TF-ThM-13, 38
Delabie, A.: TF2+AP+SE+SS-WeM-2, 27
Demelius, L.: TF1+SE+SS-ThM-4, **40**
DeMell, J.: MI+2D+TF-ThM-12, **36**
Demkov, A.: MI+2D+TF-ThM-3, **36**
Dendooven, J.: TF-ThP-14, 46
Deshmukh, N.: TF3+MS-WeM-13, **28**
Deshpande, V.: EM+MN+TF-ThM-4, 34
Detavernier, C.: TF-ThP-14, 46
Dev, P.: MI+2D+TF-ThM-12, 36
Devore, A.: BI1+AS+EM+NS+SE+TF-TuM-3, 11
Devulder, W.: PS1+TF-TuA-4, 18; TF2+AP+SE+SS-WeM-2, 27
Dhanak, V.: TF+EM-MoM-1, 5
Díaz, C.: SS+AS+TF-MoM-1, **3**
Diniz, J.: TF+EM-MoM-3, **5**
Dorst, A.: SS+AS+TF-MoM-4, **3**
Dowben, P.: TF2+2D-TuA-4, 20
Drouin, D.: PS1+TF-TuA-12, 19
Du, Q.: PS1+TF-TuA-2, 17
Dubois, J.: PS1+TF-TuA-1, 17
Dubourdieu, C.: EM+MN+TF-ThM-4, 34
Dubowsky, S.: PS1+AP+TF-WeM-10, 22
Dussart, R.: PS2+TF-WeM-10, 24
Dwivedi, V.: TF1+AP-WeA-1, 31
Dziwoki, A.: TF-ThP-3, **44**
— E —
E. Gregorczyk, K.: TF+EM-MoM-9, **5**
Eads, C.: TF+AS-ThA-1, 42
Eddy, C.: PS1+AP+TF-WeM-1, 21; PS1+AP+TF-WeM-5, 21; TF+AS-ThA-3, 42
Edel, R.: AP+PS+TF-TuA-9, **15**
Edgar, A.: TF2-WeA-11, 33
Ekerdt, J.: AP+AS+EM+HI+PS+SS+TF-TuM-12, **10**; AP+AS+EM+HI+PS+SS+TF-TuM-4, 9
Elam, J.: AP+PS+TF-TuA-10, 16; TF1+SE-WeM-5, 25
Elliott, S.: TF3+MS-WeM-12, 28
Engelmann, S.: PS1+TF-TuA-3, 18
Erickson, T.: MI+2D+TF-ThM-2, 35
Eriguchi, K.: PS2+TF-WeM-4, 23
Estrada, T.: AP+AS+EM+HI+PS+SS+TF-TuM-5, 9
Ettouri, R.: PS2+TF-WeM-10, **24**
— F —
Fan, R.: TF+EM-MoA-5, **8**
Fan, X.: SS+AS+TF-MoM-5, 4
Fang, X.: PS1+AP+TF-WeM-12, 22
Farjam, N.: TF+EM-MoA-4, 8
Farzaneh, A.: TF1+SE+SS-ThM-3, **39**

Feigelson, B.: TF2+AP+SE+SS-WeM-6, 28
Feit, C.: AP+AS+EM+HI+PS+SS+TF-TuM-6, 10; TF+AS-ThA-5, 43
Fekete, M.: SE+MN+PS+TF-WeA-3, **30**
Femi-Oyetoro, J.: TF-TuM-12, **13**
Feng, X.: AP+AS+EM+HI+PS+SS+TF-TuM-6, 10
Filler, M.: TF3+MS-WeM-13, 28
Finch, H.: TF+EM-MoM-1, 5
Fischer, A.: AP+PS+TF-TuA-1, **15**
Fonari, A.: TF3+MS-WeM-12, 28
Fong, D.: AS+2D+EM+MS+NS+SS+TF-ThA-6, 41
Fontaine, B.: PS1+TF-TuA-1, **17**
Fournel, F.: PS1+TF-TuA-11, 19
Frank, F.: SE+MN+PS+TF-WeA-7, 30
Freindl, K.: TF-ThP-3, 44
Friedman, A.: MI+2D+TF-ThM-12, 36
Frolov, S.: MI+2D+TF-ThM-10, **36**
Frost, H.: AP+2D+AS+EM+PS+SS+TF-MoM-3, 1
Fu, M.: MI+2D+TF-ThM-1, 35
Fuerst, T.: PS1+AP+TF-WeM-13, 22
Fuger, C.: SE+MN+PS+TF-WeA-10, 30
Fukasawa, M.: PS2+TF-WeM-4, 23
— G —
Gai, Z.: MI+2D+TF-ThM-1, **35**
Gammon, P.: TF+EM-MoM-1, 5
Ganesan, D.: TF+EM-MoA-6, 8
Ganesan, J.: AP+AS+EM+HI+PS+SS+TF-TuM-6, 10
Ganesan, R.: SE+MN+PS+TF-WeA-1, **30**
Gassilloud, R.: AP+2D+AS+EM+PS+SS+TF-MoM-1, 1; AP+AS+EM+HI+PS+SS+TF-TuM-3, 9; TF1+PS-FrM-2, 49
Gasvoda, R.: AP+PS+TF-TuA-1, 15
Gayle, A.: TF-TuM-10, **13**
Gemmi, M.: TF1+SE+SS-ThM-4, 40
George, S.: AP+PS+TF-TuA-12, **16**; AP+PS+TF-TuA-4, 15; AP+PS+TF-TuA-9, 15
Gertsch, J.: AP+PS+TF-TuA-12, 16
Gettler, R.: TF1+SE+SS-ThM-5, 40
Ghanekar, A.: TF+EM-MoA-1, 7
Ghosh, A.: TF+EM-MoM-10, **6**
Gianesello, F.: TF1+PS-FrM-2, 49
Giesen, D.: TF3+MS-WeM-12, 28
Gignac, L.: PS1+TF-TuA-3, 18
Girard, J.: TF2+AP+SE+SS-WeM-2, 27
Girolami, G.: TF2+AP+SE+SS-WeM-5, 27; TF-ThP-8, 45; TF-TuM-5, 12
Gittleman, B.: PS1+AP+TF-WeM-10, 22
Glaser, C.: EM+MN+TF-ThM-5, 34
Glavin, N.: TF2+2D-TuA-3, **20**
Glechner, T.: SE+MN+PS+TF-WeA-10, 30
Gogotsi, Y.: AS+2D+EM+MS+NS+SS+TF-ThA-3, 41
Gorey, T.: TF-TuM-11, **13**
Gougousi, T.: TF-ThP-1, 44
Gouraud, P.: PS1+TF-TuA-1, 17; PS2+TF-WeM-13, 25
Goya, T.: PS2+TF-WeM-4, **23**
Grasso, J.: PS1+AP+TF-WeM-11, 22
Grau-Crespo, R.: AS+2D+EM+MS+NS+SS+TF-ThA-4, 41
Graugnard, E.: AP+PS+TF-TuA-10, 16
Greenberg, B.: TF2+AP+SE+SS-WeM-6, **28**
Greer, F.: TF-TuM-12, 13
Gregorczyk, K.: TF-TuM-4, 12
Groner, M.: TF1+AP-WeA-4, **32**
Gros, V.: PS1+TF-TuA-11, 19
Gu, T.: PS1+TF-TuA-2, 17
Guan, Y.: TF2+EM-FrM-6, 49
Guo, J.: TF+EM-MoA-4, 8
Gupta, A.: BI1+AS+EM+NS+SE+TF-TuM-1, **10**
— H —
Hahn, R.: SE+MN+PS+TF-WeA-10, 30
Hajzus, J.: TF2+EM-FrM-9, 50
Hamamura, H.: PS2+TF-WeM-11, 24; PS2+TF-WeM-5, 24
Hanbicki, A.: MI+2D+TF-ThM-12, 36
Hannah, A.: TF+EM-MoM-1, 5
Hans, M.: SE+MN+PS+TF-WeA-3, 30
Harake, M.: AP+2D+AS+EM+PS+SS+TF-MoM-8, 2
Harnois, M.: TF-ThP-2, 44
Harris, Z.: SS+AS+TF-MoM-6, 4
Hartmann, H.: PS1+AP+TF-WeM-12, 22
Hausmann, D.: AP+2D+AS+EM+PS+SS+TF-MoM-5, 1
Hawker, M.: BI1+AS+EM+NS+SE+TF-TuM-3, **11**
Hayden, J.: TF2+EM-FrM-11, **51**
He, X.: TF1+SE+SS-ThM-5, 40
Head, A.: TF+AS-ThA-1, 42
Heinemans, R.: AP+2D+AS+EM+PS+SS+TF-MoM-6, 2
Heitmann, T.: TF1+SE-WeM-12, 26
Hekking, S.: TF+AP-ThM-12, 39
Held, G.: AS+2D+EM+MS+NS+SS+TF-ThA-4, **41**
Herman, A.: SS+AS+TF-MoM-5, 4
Herman, G.: SS+AS+TF-MoM-5, **4**
Hill, A.: TF-TuM-10, 13
Hirle, A.: SE+MN+PS+TF-WeA-10, 30
Hitchcock, D.: PS1+AP+TF-WeM-6, 21
Hite, J.: PS1+AP+TF-WeM-5, 21; TF+AS-ThA-3, 42
Hoffman, J.: TF-TuM-10, 13
Hofmann, S.: TF2+2D-TuA-1, **20**
Hofmann, T.: TF+EM-MoA-3, 7
Högberg, H.: TF2+EM-FrM-8, 50
Homayounfar, S.: TF+EM-MoA-6, **8**
Hong, H.: AS+2D+EM+MS+NS+SS+TF-ThA-6, 41
Hopstaken, M.: PS1+TF-TuA-3, 18; PS2+TF-WeM-12, 24
Hori, M.: PS2+TF-WeM-11, 24; PS2+TF-WeM-5, 24
Hossain, M.: TF1+PS-FrM-3, 49
Hossein, A.: EM+MN+TF-ThM-6, 35
Hsiao, C.: TF-ThP-19, **47**
Hu, J.: PS1+TF-TuA-2, 17
Hu, T.: TF+AS-ThA-1, **42**
Huang, S.: MI+2D+TF-ThM-1, 35
Huber, M.: LS2+2D+AS+TF-TuA-9, 17
Hues, S.: AP+PS+TF-TuA-10, 16
Hughes, B.: TF1+AP-WeA-4, 32
Hummel Cioldin, F.: TF-ThP-4, 45
Hunold, O.: SE+MN+PS+TF-WeA-10, 30
Hussey, D.: LS2+2D+AS+TF-TuA-9, 17
— I —
I-Cheng Hsu, S.: TF1+SE-WeM-11, 26
Ihlefeld, J.: TF+EM-MoM-4, 5
Ilhom, S.: PS1+AP+TF-WeM-11, **22**; TF-ThP-15, 47
Ingram, D.: MI+2D+TF-ThM-2, 35
Ishikawa, K.: PS2+TF-WeM-11, 24; PS2+TF-WeM-5, **24**
Izawa, M.: PS2+TF-WeM-11, 24; PS2+TF-WeM-5, 24
— J —
Jacobs, A.: TF2+AP+SE+SS-WeM-6, 28
Jacobson, D.: PS1+AP+TF-WeM-10, 22
Jaffal, M.: AP+2D+AS+EM+PS+SS+TF-MoM-1, 1
Jahrman, E.: TF+AS-ThA-4, 42
Jain, H.: TF1+SE-WeM-13, **26**
Janek, J.: PS1+AP+TF-WeM-12, 22
Jaramillo, R.: TF3+MS-WeM-10, **28**
Jean, B.: TF1+SE-WeM-4, **25**
Jessup, D.: SS+AS+TF-MoM-6, **4**
Jiang, K.: EM+MN+TF-ThM-3, 34
Jin, R.: MI+2D+TF-ThM-1, 35
Joanni, E.: TF+EM-MoM-3, 5
Job, A.: PS1+AP+TF-WeM-13, **22**
Johnson, M.: PS1+AP+TF-WeM-1, 21; PS1+AP+TF-WeM-5, 21; TF+AS-ThA-3, 42
Johnson, S.: PS1+AP+TF-WeM-5, 21; TF+AS-ThA-3, 42
Jones, L.: TF+EM-MoM-1, 5
Joshi, K.: TF-ThP-15, 47
Jun, Y.: TF-ThP-9, 45
Jung, E.: TF-ThP-16, **47**
— K —
Kainz, C.: SE+AS+BI+SS+TF-ThM-4, **37**; SE+MN+PS+TF-WeA-7, 30
Kaiser, H.: TF1+SE-WeM-12, 26
Kalanyan, B.: TF+AS-ThA-4, **42**; TF1+AP-WeA-1, **31**
Kalinin, S.: MS+AP+AS+TF-MoA-5, 7
Kan, F.: SE+AS+BI+SS+TF-ThM-12, 38
Kang, M.: PS1+TF-TuA-2, 17
Kang, S.: TF1+PS-FrM-4, 49
Kapadia, R.: TF+EM-MoA-1, 7
Kaplar, R.: EM+MN+TF-ThM-5, 34
Karimi Aghda, S.: AS+2D+EM+MS+NS+SS+TF-ThA-5, 41
Katoch, J.: LS2+2D+AS+TF-TuA-7, **16**
Kawakami, R.: MI+2D+TF-ThM-5, **36**
Kaye, A.: TF+AS-ThA-6, **43**
Keene, J.: TF1+AP-WeA-4, 32
Kemal Okyay, A.: TF-ThP-15, 47
Keovisai, M.: PS1+TF-TuA-11, 19
Kern, K.: LS2+2D+AS+TF-TuA-10, 17
Kersell, H.: SS+AS+TF-MoM-5, 4
Kessels, E.: AP+2D+AS+EM+PS+SS+TF-MoM-6, 2; TF1+AP-WeA-3, 32; TF2+AP+SE+SS-WeM-4, **27**
Kessels, W.: AP+2D+AS+EM+PS+SS+TF-MoM-5, 1
Khachariya, D.: TF2+EM-FrM-6, **49**
Kiaghadi, A.: TF+EM-MoA-6, 8
Kiener, D.: SE+AS+BI+SS+TF-ThM-4, 37
Kienzle, P.: LS2+2D+AS+TF-TuA-9, 17
Killelea, D.: SS+AS+TF-MoM-4, 3
Kim, H.: TF-ThP-5, 45; TF-ThP-6, 45
Kim, N.: TF1+PS-FrM-4, 49; TF-ThP-9, 45
Kim, S.: TF1+PS-FrM-4, **49**; TF-ThP-9, **45**
Kim, Y.: LS2+2D+AS+TF-TuA-9, 17
King, S.: AP+2D+AS+EM+PS+SS+TF-MoM-9, 2; TF-ThP-11, 46
Kirnbauer, A.: SE+MN+PS+TF-WeA-9, **30**
Kirste, R.: TF2+EM-FrM-6, 49
Klimov, N.: LS2+2D+AS+TF-TuA-9, 17
Ko, W.: MI+2D+TF-ThM-1, 35
Kobayashi, H.: AP+PS+TF-TuA-3, 15
Kodama, Y.: PS2+TF-WeM-4, 23
Koenig, H.: TF1+SE+SS-ThM-5, 40
Kohn, E.: TF2+EM-FrM-6, 49
Kolozsvari, S.: SE+MN+PS+TF-WeA-12, 31
Kolozsvári, S.: SE+AS+BI+SS+TF-ThM-3, 37; SE+MN+PS+TF-WeA-9, 30
Korecki, J.: TF-ThP-3, 44
Kothapally, S.: TF2-WeA-10, 33
Kotru, S.: TF2-WeA-10, 33
Kozen, A.: TF-TuM-4, 12
Krogstad, J.: TF2+AP+SE+SS-WeM-5, 27
Krüger, F.: PS1+TF-TuA-10, **19**
Kumar, U.: TF+AS-ThA-5, 43
Kundu, S.: PS1+TF-TuA-7, **18**
Kushner, M.: PS1+TF-TuA-10, 19
— L —
LaManna, J.: LS2+2D+AS+TF-TuA-9, 17
Lang, A.: TF2+EM-FrM-9, 50

Author Index

Lapras, V.: PS1+TF-TuA-11, 19
Lavoie, C.: PS2+TF-WeM-12, 24
Lawrence, B.: TF-ThP-12, 46
Lazzarino, F.: PS1+TF-TuA-4, 18; PS1+TF-TuA-7, 18
Le Brun, N.: PS2+TF-WeM-13, **25**
LeDuc, H.: TF-TuM-12, 13
Lee, C.: TF-ThP-17, **47**
Lee, H.: PS1+TF-TuA-10, 19
Lee, J.: SE+AS+BI+SS+TF-ThM-12, **38**
Lee, Y.: TF-ThP-5, **45**; TF-ThP-6, 45
Lefaucheux, P.: PS2+TF-WeM-10, 24
Lemaire, P.: AP+2D+AS+EM+PS+SS+TF-MoM-5, 1
Lenef, J.: TF+EM-MoA-4, 8
Lenert, A.: TF-TuM-10, 13
Lengers, R.: AP+2D+AS+EM+PS+SS+TF-MoM-6, 2
Leusink, G.: AP+2D+AS+EM+PS+SS+TF-MoM-4, 1; AP+PS+TF-TuA-7, **15**
Lewis, D.: TF1+AP-WeA-4, 32
Lewis, J.: TF1+SE-WeM-11, **26**
Li, C.: PS1+AP+TF-WeM-13, 22
Li, J.: TF1+AP-WeA-4, 32
Liao, B.: TF-ThP-19, 47
Liaw, P.: SS+AS+TF-MoM-5, 4
Liberman, V.: PS1+TF-TuA-2, 17
Lill, T.: AP+PS+TF-TuA-1, 15
Lin, J.: SE+AS+BI+SS+TF-ThM-6, **37**
Linford, M.: TF-ThP-12, **46**
Litzius, K.: LS2+2D+AS+TF-TuA-10, **17**
Liu, A.: BI1+AS+EM+NS+SE+TF-TuM-1, 10
Liu, B.: PS1+AP+TF-WeM-2, **21**
Liu, T.: AP+2D+AS+EM+PS+SS+TF-MoM-8, **2**
Liu, Y.: MS+AP+AS+TF-MoA-5, **7**
Lively, R.: TF1+SE-WeM-4, 25
Livingston, K.: TF1+AP-WeA-4, 32
Lizarbe, A.: TF-ThP-12, 46
Löfler, L.: SE+MN+PS+TF-WeA-3, 30
Long, D.: TF-TuM-4, 12
Losego, M.: TF1+SE-WeM-1, **25**; TF1+SE-WeM-4, 25; TF1+SE-WeM-6, 26
Lou, B.: SE+AS+BI+SS+TF-ThM-12, 38
Ludwig, K.: PS1+AP+TF-WeM-5, 21; TF+AS-ThA-3, 42
Lukin, D.: NS3+EM+TF-MoM-10, **3**
Lutker-Lee, K.: AP+2D+AS+EM+PS+SS+TF-MoM-3, 1
Lyu, Z.: SS+AS+TF-MoM-5, 4
— M —
Maccaferri, N.: EM+MN+TF-ThM-6, 35
Macco, B.: TF1+AP-WeA-3, 32
Machado, P.: TF1+SE+SS-ThM-1, 39
Mackus, A.: AP+2D+AS+EM+PS+SS+TF-MoM-5, 1; AP+2D+AS+EM+PS+SS+TF-MoM-6, 2
Maeda, K.: PS2+TF-WeM-11, 24; PS2+TF-WeM-5, 24
Maindron, T.: AP+AS+EM+HI+PS+SS+TF-TuM-3, 9
Major, G.: TF-ThP-12, 46
Maloney, P.: TF-TuM-13, 14
Mameli, A.: TF2+AP+SE+SS-WeM-4, 27
Mane , A.: TF1+SE-WeM-5, 25
Mane, A.: AP+PS+TF-TuA-10, 16
Mantoux, A.: TF1+PS-FrM-2, 49
Marchack, N.: PS2+TF-WeM-12, **24**
Maria, J.: TF1+PS-FrM-3, 49; TF1+SE+SS-ThM-6, 40; TF2+EM-FrM-10, 50; TF2+EM-FrM-11, 51
Martinez, M.: TF1+AP-WeA-4, 32
Martinson, A.: AP+AS+EM+HI+PS+SS+TF-TuM-10, **10**
Maslar, J.: TF+AS-ThA-4, 42; TF1+AP-WeA-1, 31
Maudet, F.: EM+MN+TF-ThM-4, 34
Mawby, P.: TF+EM-MoM-1, 5
Mayrhofer, P.: SE+AS+BI+SS+TF-ThM-3, 37; SE+MN+PS+TF-WeA-12, 31; SE+MN+PS+TF-WeA-9, 30
Mazet, L.: AP+AS+EM+HI+PS+SS+TF-TuM-3, 9
McChesney, J.: AS+2D+EM+MS+NS+SS+TF-ThA-6, **41**
McCluskey, P.: TF+EM-MoM-9, 5
McDowell, N.: AP+PS+TF-TuA-3, **15**
McGregor, M.: BI1+AS+EM+NS+SE+TF-TuM-5, **11**
McGuinness, E.: TF1+SE-WeM-4, 25
McIlwaine, N.: TF1+PS-FrM-3, **49**
McKeown, B.: TF2+AP+SE+SS-WeM-2, 27
McLamb, M.: TF+EM-MoA-3, **7**
Mecouch, W.: TF2+EM-FrM-6, 49
Merkx, M.: AP+2D+AS+EM+PS+SS+TF-MoM-5, 1; AP+2D+AS+EM+PS+SS+TF-MoM-6, **2**
Meyer, M.: TF-TuM-13, **14**
Miceli, A.: TF-ThP-13, **46**
Miller, P.: PS1+TF-TuA-2, 17
Mimura, T.: TF+EM-MoM-4, 5
Mione, M.: TF2+AP+SE+SS-WeM-4, 27
Mita, S.: TF2+EM-FrM-6, 49
Mitrovic, I.: TF+EM-MoM-1, **5**
Miyazoe, H.: PS1+TF-TuA-3, 18
Miyoshi, N.: AP+PS+TF-TuA-3, 15
Moffitt, C.: TF-ThP-10, **46**
Mohammad, A.: PS1+AP+TF-WeM-11, 22; TF-ThP-15, **47**
Montgomery-Smith, S.: TF1+SE+SS-ThM-5, 40
Moody, B.: TF2+EM-FrM-6, 49
Moridi, M.: TF-ThP-20, 47
Moryson, Y.: PS1+AP+TF-WeM-12, **22**
Moser, D.: TF1+AP-WeA-1, 31
Murdzek, J.: AP+PS+TF-TuA-4, 15
Murphy, J.: TF+AS-ThA-2, **42**
Murphy, R.: LS2+2D+AS+TF-TuA-9, 17
Myers-Ward, R.: TF2+EM-FrM-9, 50
— N —
Nallan, H.: AP+AS+EM+HI+PS+SS+TF-TuM-12, 10
Nam, S.: PS1+TF-TuA-10, 19
Nam, T.: AP+PS+TF-TuA-9, 15
Napari, M.: TF+AP-ThM-10, **38**
Naumov, I.: MI+2D+TF-ThM-12, 36
Nepal, N.: TF+AS-ThA-3, 42
Nguyen, T.: PS2+TF-WeM-11, **24**; PS2+TF-WeM-5, 24
Nnaji, M.: PS1+AP+TF-WeM-6, **21**
Nordlander, J.: TF2+EM-FrM-10, **50**; TF2+EM-FrM-11, 51
Not, J.: AP+AS+EM+HI+PS+SS+TF-TuM-3, **9**
Nuwayhid, B.: TF-TuM-4, **12**
Nyns, L.: TF2+AP+SE+SS-WeM-2, **27**
— O —
Okyay, A.: PS1+AP+TF-WeM-11, 22
Ondračka, P.: AS+2D+EM+MS+NS+SS+TF-ThA-5, 41; SE+MN+PS+TF-WeA-3, 30
Ontaneda, J.: AS+2D+EM+MS+NS+SS+TF-ThA-4, 41
Orefice, A.: PS2+TF-WeM-12, 24
Orson, K.: SS+AS+TF-MoM-6, 4
Ott, V.: SE+AS+BI+SS+TF-ThM-3, **37**
Otto, S.: PS1+AP+TF-WeM-12, 22
— P —
Pallem, V.: TF2+AP+SE+SS-WeM-2, 27
Papalia, J.: PS1+TF-TuA-3, 18
Paquette, M.: AP+2D+AS+EM+PS+SS+TF-MoM-9, **2**
Paranamana, N.: TF1+SE+SS-ThM-5, **40**; TF1+SE-WeM-12, 26
Park, C.: TF-ThP-16, 47
Park, N.: AS+2D+EM+MS+NS+SS+TF-ThA-1, **41**
Parlanti, P.: TF1+SE+SS-ThM-4, 40
Parmigiani, L.: PS2+TF-WeM-13, 25
Parsons, Z.: AP+AS+EM+HI+PS+SS+TF-TuM-6, 10
Partridge, J.: AP+PS+TF-TuA-4, **15**
Patel, D.: PS1+AP+TF-WeM-10, **22**
Pathak, R.: TF1+SE-WeM-5, **25**
Patouillard, J.: TF1+PS-FrM-2, **49**
Patterer, L.: AS+2D+EM+MS+NS+SS+TF-ThA-5, **41**
Paul, R.: TF2-WeA-10, **33**
Pavlidis, S.: TF2+EM-FrM-6, 49
Pech, S.: TF-ThP-9, 45
Pedersen, H.: TF2+EM-FrM-8, 50
Peissker, T.: TF2+AP+SE+SS-WeM-2, 27
Penley, D.: TF1+AP-WeA-2, **31**
Pennachio, D.: TF2+EM-FrM-9, **50**
Peterson, J.: TF+EM-MoM-4, **5**
Philippe, H.: PS2+TF-WeM-10, 24
Phillips, J.: TF2+2D-TuA-4, 20
Phung, J.: PS2+TF-WeM-10, 24
Phung, N.: TF+AP-ThM-13, 39
Pilz, J.: TF-ThP-20, **47**
Pimenta-Barros, P.: PS2+TF-WeM-3, 23
Pinna, N.: TF-TuM-6, **13**
Pinnepalli, S.: AP+2D+AS+EM+PS+SS+TF-MoM-9, 2
Plummer, E.: MI+2D+TF-ThM-1, 35
Pohler, M.: SE+AS+BI+SS+TF-ThM-4, 37; SE+MN+PS+TF-WeA-11, 31; SE+MN+PS+TF-WeA-7, 30
Polcik, P.: SE+AS+BI+SS+TF-ThM-3, 37; SE+MN+PS+TF-WeA-10, 30
Poodt, P.: TF1+SE-WeM-13, 26
Popescu, C.: PS1+TF-TuA-2, 17
Porter, L.: EM+MN+TF-ThM-3, **34**
Porzier, C.: PS1+TF-TuA-11, 19
Posseme, N.: AP+2D+AS+EM+PS+SS+TF-MoM-1, 1; PS1+TF-TuA-1, 17; PS1+TF-TuA-11, 19; PS2+TF-WeM-3, 23
Povinelli, M.: TF+EM-MoA-1, **7**
Powalla, L.: LS2+2D+AS+TF-TuA-10, 17
Primetzhofer, D.: SE+MN+PS+TF-WeA-3, 30
— R —
Ragonesi, J.: TF1+AP-WeA-4, 32
Ramm, J.: SE+MN+PS+TF-WeA-10, 30
Rathkanthiwar, S.: TF2+EM-FrM-6, 49
Ravi, A.: TF1+SE-WeM-11, 26
Raybin, J.: TF+AS-ThA-2, 42
Raynaud, C.: TF1+PS-FrM-2, 49
Rayner, B.: PS1+AP+TF-WeM-2, 21
Raza, H.: TF-TuM-6, 13
Reddy, P.: TF2+EM-FrM-6, 49
Reichardt, S.: EM+MN+TF-ThM-6, 35
Reinke, P.: SS+AS+TF-MoM-6, 4
Ren, Y.: TF1+SE-WeM-4, 25
Renz, A.: TF+EM-MoM-1, 5
Reyes, G.: BI1+AS+EM+NS+SE+TF-TuM-3, 11
Richardson, K.: PS1+TF-TuA-2, 17
Riedl, H.: SE+AS+BI+SS+TF-ThM-3, 37; SE+MN+PS+TF-WeA-10, **30**
Rios, C.: PS1+TF-TuA-2, 17
Ritala, M.: AP+AS+EM+HI+PS+SS+TF-TuM-1, **9**
Rival, A.: PS1+TF-TuA-1, 17
Robert, R.: AP+2D+AS+EM+PS+SS+TF-MoM-3, **1**
Roberto Silva, A.: TF-ThP-4, 45
Roberts, C.: PS1+TF-TuA-2, 17
Robinson, J.: MI+2D+TF-ThM-12, 36
Robinson, P.: PS1+TF-TuA-2, 17
Robinson, S.: LS2+2D+AS+TF-TuA-9, **17**
Robinson, Z.: TF+AS-ThA-3, 42

Author Index

Rodgers, M.: TF1+AP-WeA-4, 32
Rodriguez, D.: TF2-WeA-11, **33**
Rohnke, M.: PS1+AP+TF-WeM-12, 22
Roozeboom, F.: TF2+AP+SE+SS-WeM-4, 27
Rorem, B.: TF+EM-MoA-4, 8
Rosenberg, S.: PS1+AP+TF-WeM-5, 21; TF+AS-ThA-3, 42
Rothman, A.: TF2+AP+SE+SS-WeM-1, **27**
Routzahn, A.: AP+PS+TF-TuA-1, 15
Ruault, P.: PS1+TF-TuA-11, 19
Rubloff, G.: TF-TuM-3, 12; TF-TuM-4, 12
Ruel, S.: PS2+TF-WeM-3, **23**
Rummel, B.: EM+MN+TF-ThM-5, **34**
Ruzic, D.: PS1+AP+TF-WeM-10, 22
— S —
Sallaz, V.: TF+EM-MoM-9, 5
Sallés, P.: TF1+SE+SS-ThM-1, 39
Sandoval, T.: AP+2D+AS+EM+PS+SS+TF-MoM-5, 1; AP+2D+AS+EM+PS+SS+TF-MoM-6, 2
Sankaran, M.: EM+MN+TF-ThM-6, 35
Sankaranarayanan, S.: MS+AP+AS+TF-MoA-3, **7**
Saringer, C.: SE+AS+BI+SS+TF-ThM-4, 37
Sartory, B.: SE+MN+PS+TF-WeA-11, 31
Sato, T.: PS2+TF-WeM-1, **23**
Schäfer, T.: SS+AS+TF-MoM-4, 3
Schalk, N.: SE+AS+BI+SS+TF-ThM-4, 37; SE+MN+PS+TF-WeA-11, 31; SE+MN+PS+TF-WeA-7, **30**
Schauermann, S.: SS+AS+TF-MoM-3, **3**
Schell, N.: SE+AS+BI+SS+TF-ThM-4, 37
Schmid, B.: SE+MN+PS+TF-WeA-12, **31**
Schmidt, M.: SS+AS+TF-MoM-3, 3
Schneider, J.: AS+2D+EM+MS+NS+SS+TF-ThA-5, 41; SE+MN+PS+TF-WeA-3, 30
Schroeder, C.: SS+AS+TF-MoM-3, 3
Schutz, G.: LS2+2D+AS+TF-TuA-10, 17
Seal, S.: TF+AS-ThA-5, 43
Shah, V.: TF+EM-MoM-1, 5
Shahine, I.: TF-ThP-2, **44**
Shalaginov, M.: PS1+TF-TuA-2, 17
Sharma, S.: TF2+EM-FrM-8, 50
Sharps, P.: EM+MN+TF-ThM-5, 34
Shatruk, M.: TF2+2D-TuA-4, 20
Shenderova, O.: EM+MN+TF-ThM-6, 35
Shevate, R.: TF1+SE-WeM-5, 25
Shi, J.: TF1+SE-WeM-11, 26
Shinoda, K.: PS2+TF-WeM-11, 24; PS2+TF-WeM-5, 24
Shirodkar, S.: MI+2D+TF-ThM-12, 36
Shrewsbury, B.: TF+EM-MoA-1, 7
Shrivastav, S.: TF2+AP+SE+SS-WeM-5, 27; TF-TuM-5, 12
Shuchi, N.: TF+EM-MoA-3, 7
Sibener, S.: TF+AS-ThA-2, 42
Sierakowski, K.: TF2+EM-FrM-6, 49
Sims, J.: AP+PS+TF-TuA-1, 15
Sinani, T.: TF-ThP-20, 47
Singh, J.: BI1+AS+EM+NS+SE+TF-TuM-4, **11**
Singh, V.: TF-ThP-11, 46
Sinha, J.: TF2+AP+SE+SS-WeM-2, 27
Sinnott, S.: SS+AS+TF-MoM-8, **4**
Sitar, Z.: TF2+EM-FrM-10, 50; TF2+EM-FrM-6, 49
Skidmore, C.: TF1+SE+SS-ThM-6, **40**
Smith, A.: MI+2D+TF-ThM-2, 35
Smith, T.: EM+MN+TF-ThM-5, 34
Soares, J.: AP+PS+TF-TuA-10, **16**
Sortino, E.: AP+PS+TF-TuA-12, 16
Souqui, L.: TF2+AP+SE+SS-WeM-5, 27; TF2+EM-FrM-8, **50**; TF-ThP-8, 45; TF-TuM-5, **12**
Souriau, L.: PS1+TF-TuA-4, 18; PS1+TF-TuA-9, 18
Spiridis, N.: TF-ThP-3, 44
Stacchiola, D.: TF+AS-ThA-1, 42
Stafford, N.: TF2+AP+SE+SS-WeM-2, 27
Stagon, S.: TF-ThP-13, 46
Stanford, M.: TF2-WeA-7, **32**
Stark, A.: SE+AS+BI+SS+TF-ThM-4, 37
Steenman, W.: TF1+AP-WeA-4, 32
Stein, S.: TF2+EM-FrM-6, 49
Steiner, A.: TF1+SE-WeM-6, 26
Steinfeldt, J.: EM+MN+TF-ThM-5, 34
Steingrimsson, B.: SS+AS+TF-MoM-5, 4
Stephen, G.: MI+2D+TF-ThM-12, 36
Stewart, D.: TF-TuM-3, 12
Stinnett, T.: SE+AS+BI+SS+TF-ThM-6, 37
Stinson, V.: TF+EM-MoA-3, 7
Stowell, M.: PS1+AP+TF-WeM-10, 22
Strangi, G.: EM+MN+TF-ThM-6, 35
Stroud, R.: TF2+EM-FrM-9, 50
Stueber, M.: SE+AS+BI+SS+TF-ThM-3, 37
Sulchek, T.: BI1+AS+EM+NS+SE+TF-TuM-1, 10
Sun, K.: MI+2D+TF-ThM-2, 35
Sun, L.: MI+2D+TF-ThM-12, 36
Swearingen, H.: PS1+AP+TF-WeM-10, 22
Swerts, J.: TF2+AP+SE+SS-WeM-2, 27
Szymanski, D.: TF2+EM-FrM-6, 49
— T —
Tabachnick, C.: PS1+TF-TuA-3, 18
Tae, H.: TF-ThP-16, 47
Tang, J.: EM+MN+TF-ThM-3, 34
Tapily, K.: AP+2D+AS+EM+PS+SS+TF-MoM-4, 1
Taylor, C.: PS1+AP+TF-WeM-13, 22
Taylor, P.: MI+2D+TF-ThM-12, 36
Tekin, S.: TF+EM-MoM-1, 5
Teplyakov, A.: AP+PS+TF-TuA-11, **16**
Tessier, P.: TF-ThP-2, 44
Tezsevin, I.: AP+2D+AS+EM+PS+SS+TF-MoM-5, 1; AP+2D+AS+EM+PS+SS+TF-MoM-6, 2
Thapa, R.: AP+2D+AS+EM+PS+SS+TF-MoM-9, 2
Thompson, F.: SE+AS+BI+SS+TF-ThM-5, 37
Thoueille, P.: PS2+TF-WeM-3, 23
Tillocher, T.: PS2+TF-WeM-10, 24
Tiwari, S.: TF3+MS-WeM-12, 28
Tkadletz, M.: SE+AS+BI+SS+TF-ThM-4, 37; SE+MN+PS+TF-WeA-11, **31**; SE+MN+PS+TF-WeA-7, 30
Trejo, O.: TF1+AP-WeA-2, 31
Trenary, M.: SS+AS+TF-MoM-10, 4
Troglia, A.: SE+AS+BI+SS+TF-ThM-13, **38**
Trolier-McKinstry, S.: TF2+EM-FrM-11, 51
Truffier-Boutry, D.: PS1+TF-TuA-11, 19
Tsousis, D.: TF2+AP+SE+SS-WeM-1, 27
Tweedie, J.: TF2+EM-FrM-6, 49
— U —
Ulrich, S.: SE+AS+BI+SS+TF-ThM-3, 37
Unger, K.: TF1+SE+SS-ThM-4, 40
Upadhyay, S.: MI+2D+TF-ThM-2, **35**
Urabe, K.: PS2+TF-WeM-4, 23
Usov, I.: TF2-WeA-11, 33
— V —
Valenti, A.: AP+2D+AS+EM+PS+SS+TF-MoM-4, **1**
Valentine, B.: MS+AP+AS+TF-MoA-10, **7**
Valizadeh, R.: TF+EM-MoM-1, 5
Vallee, C.: AP+2D+AS+EM+PS+SS+TF-MoM-1, **1**
Vallée, C.: AP+2D+AS+EM+PS+SS+TF-MoM-3, 1; AP+2D+AS+EM+PS+SS+TF-MoM-4, 1; TF+AP-ThM-12, 39
van de Groep, J.: SE+AS+BI+SS+TF-ThM-13, 38
van de Poll, M.: SE+AS+BI+SS+TF-ThM-13, 38; TF1+AP-WeA-3, **32**
Van Dijck, C.: EM+MN+TF-ThM-4, **34**
van Helvoirt, C.: TF+AP-ThM-13, **39**
Vandalon, V.: TF2+AP+SE+SS-WeM-4, 27
Vaninger, M.: TF1+SE-WeM-12, 26
Ventrice, C.: AP+2D+AS+EM+PS+SS+TF-MoM-4, 1
Vidal, M.: TF+EM-MoM-3, 5
Vitale, S.: PS1+TF-TuA-2, **17**
Vodnik, D.: TF2-WeA-11, 33
Vogel, E.: PS1+AP+TF-WeM-6, 21
Voiron, F.: TF+EM-MoM-9, 5
Vuckovic, J.: NS3+EM+TF-MoM-10, 3
— W —
W. Rubloff, G.: TF+EM-MoM-9, 5
Wajda, C.: AP+2D+AS+EM+PS+SS+TF-MoM-4, 1
Waldl, H.: SE+MN+PS+TF-WeA-11, 31
Walker, A.: AP+AS+EM+HI+PS+SS+TF-TuM-5, **9**
Walton, S.: PS1+AP+TF-WeM-1, 21; PS1+AP+TF-WeM-5, **21**; TF+AS-ThA-3, 42
Wang, P.: TF2+2D-TuA-4, 20
Way, J.: PS1+AP+TF-WeM-13, 22
Weigand, M.: LS2+2D+AS+TF-TuA-10, 17
Weigandt, K.: LS2+2D+AS+TF-TuA-9, 17
Wells, B.: TF-ThP-15, 47
Werbrouck, A.: TF-ThP-14, **46**
Wheeler, V.: PS1+AP+TF-WeM-5, 21
Willis, B.: PS1+AP+TF-WeM-11, 22; TF-ThP-15, 47
Wintz, S.: LS2+2D+AS+TF-TuA-10, 17
Wirtz, L.: EM+MN+TF-ThM-6, 35
Wojcik, T.: SE+AS+BI+SS+TF-ThM-3, 37; SE+MN+PS+TF-WeA-10, 30
Wojtecki, R.: AP+2D+AS+EM+PS+SS+TF-MoM-10, **2**
Wolden, C.: PS1+AP+TF-WeM-13, 22
Wolf, C.: LS2+2D+AS+TF-TuA-9, 17
Wollmershauser, J.: TF2+AP+SE+SS-WeM-6, 28
Wong, M.: EM+MN+TF-ThM-1, **34**
Woodward, J.: PS1+AP+TF-WeM-5, 21; TF+AS-ThA-3, **42**
Wosik, J.: SE+MN+PS+TF-WeA-11, 31
Wyatt, B.: TF2+2D-TuA-4, 20
Wyatt, Q.: TF1+SE-WeM-12, 26
— Y —
Yang, R.: TF2-WeA-8, **32**
Yang, X.: AP+AS+EM+HI+PS+SS+TF-TuM-12, 10; AP+AS+EM+HI+PS+SS+TF-TuM-4, **9**
Yang, Y.: MI+2D+TF-ThM-1, 35
Yates, L.: EM+MN+TF-ThM-5, 34
Yazdani, S.: TF2+2D-TuA-4, **20**
Yeghoyan, T.: AP+2D+AS+EM+PS+SS+TF-MoM-1, 1
Yeom, G.: TF-ThP-5, 45; TF-ThP-6, 45
Yokogawa, K.: PS2+TF-WeM-11, 24; PS2+TF-WeM-5, 24
Young, M.: TF1+SE+SS-ThM-5, 40; TF1+SE-WeM-12, **26**
Yu, K.: AP+2D+AS+EM+PS+SS+TF-MoM-4, 1
Yu, P.: AP+2D+AS+EM+PS+SS+TF-MoM-5, **1**; AP+2D+AS+EM+PS+SS+TF-MoM-6, 2
— Z —
Zaizen, Y.: PS2+TF-WeM-4, 23
Zauner, L.: SE+MN+PS+TF-WeA-10, 30
Zhang, Y.: PS1+TF-TuA-2, 17
Zhao, K.: MI+2D+TF-ThM-1, 35
Zhu, W.: TF2+EM-FrM-11, 51
Zou, Q.: MI+2D+TF-ThM-1, 35